

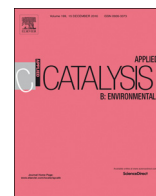


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# Applied Catalysis B: Environmental

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## The alkali resistance of CuNbTi catalyst for selective reduction of NO by NH<sub>3</sub>: A comparative investigation with VWTi catalyst

Xiaoxiang Wang<sup>a</sup>, Qiliang Cong<sup>a</sup>, Liang Chen<sup>a</sup>, Yun Shi<sup>b</sup>, Yao Shi<sup>a</sup>, Sujing Li<sup>a,\*</sup>, Wei Li<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Institute of Industrial Ecology and Environment, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

<sup>b</sup> Zhejiang University of Science & Technology, Hangzhou 310023, China

### ARTICLE INFO

#### Keywords:

CuNbTi catalyst  
VWTi catalyst  
NH<sub>3</sub>-SCR  
Alkali metal resistance  
Synergetic effect

### ABSTRACT

The alkali metal poisoned CuNbTi and VWTi catalysts were prepared by wetness impregnation method. Poisoning effects of various K<sub>2</sub>O mass ratios (0.1%–2%) on CuNbTi and VWTi catalysts were studied, respectively. CuNbTi exhibited an excellent alkali metal resistance that 2%K<sub>2</sub>O-CuNbTi still remained 80% NO<sub>x</sub> conversion efficiency and 98% N<sub>2</sub> selectivity while 2%K<sub>2</sub>O-VWTi was completely deactivated. Moreover, different alkali metals (K, Na, Ca, Mg) with the same molar ratio were doped on CuNbTi. The poisoned degree followed the order: K<sub>2</sub>O > Na<sub>2</sub>O > CaO > MgO. Then 2%K<sub>2</sub>O-CuNbTi and 2%K<sub>2</sub>O-VWTi were selected for follow-up study. To understand the poisoning mechanism, further investigations were performed by SEM, XRD, N<sub>2</sub>-physisorption, XPS, EPR, NH<sub>3</sub>-TPD, Py-IR, H<sub>2</sub>-TPR, in situ DRIFTS characterizations and DFT calculations. The particle of CuNbTi and VWTi agglomerated and the surface area decreased after 2%K<sub>2</sub>O loading. Loss of acid sites and drop of reducibility resulted in the deactivation of 2%K<sub>2</sub>O-VWTi. By contrast, experimental and computational results indicated that the alkali resistance of 2%K<sub>2</sub>O-CuNbTi was mainly due to the interaction between Ti<sub>2</sub>NbO<sub>x</sub> support and K atoms that K atoms were preferentially bound to Nb–OH and Nb=O with a lower bonding energy of –2.33 eV–2.83 eV when Cu atoms were coordinated to Ti=O with a binding energy of –1.54 eV. This protected the active copper species from linking to K<sub>2</sub>O and the weak acid sites were preserved with the increasing isolated Cu<sup>2+</sup>. Ti<sub>2</sub>NbO<sub>x</sub> weakened the impact of potassium on NH<sub>3</sub> adsorbing over the catalyst while the preserved copper species provided adsorption sites and redox ability for NH<sub>3</sub>-SCR reaction. Hence, the synergetic effect of copper and niobium species contributed to the alkali metal resistance. Ti<sub>2</sub>NbO<sub>x</sub> trapped the potassium and retained active copper species over 2%K<sub>2</sub>O-CuNbTi catalyst while potassium deactivated both TiO<sub>2</sub> and active vanadium species on 2%K<sub>2</sub>O-VWTi catalyst. Meanwhile, both Eley-Rideal (E-R) and Langmuir-Hinshelwood (H-L) mechanisms with adsorbed NH<sub>3</sub> coordinated to the Lewis acid sites and bidentate nitrate as the dominating intermediate species existed during the NH<sub>3</sub>-SCR reaction procedure over 2%K<sub>2</sub>O-CuNbTi at 225 °C.

### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) in the air could cause a series of hazardous environmental pollution problems, such as acid rain, ozone depletion and photochemical smog etc. [1] Selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> (NH<sub>3</sub>-SCR) is one of efficient technologies for NO<sub>x</sub> abatement [2] and the catalyst is the core of this technology. Different catalysts were developed for different applications, including stationary sources and mobile sources [3]. Especially, for the stationary sources, which included coal fired power plants, biomass combustion plants and solid-waste incineration plants, they would emit large amount of flue gas containing complex components, such as NO<sub>x</sub>, SO<sub>x</sub>, alkaline metals

[1,4]. However, alkaline earth metals of potassium (K), sodium (Na), magnesium (Mg) and calcium (Ca) in the flue gas could deactivate the SCR catalysts seriously [5]. Therefore, the effect of alkali metals on the SCR catalyst must be taken into consideration in NH<sub>3</sub>-SCR catalytic research.

The poisoning effects of alkali on the SCR catalysts have been extensively investigated. Most scholars have studied the influence of alkali metals on traditional VW(Mo)Ti catalysts. Chen [6] proposed that the poisoning degree of different alkali metals on the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> was K > Na > Mg. Tang [7] suggested that sodium coordinated with vanadia species and decreased the acid sites and reducibility of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>. Li et al. [8] compared the effects of different calcium salts on the

\* Corresponding authors.

E-mail addresses: [sujing-li@zju.edu.cn](mailto:sujing-li@zju.edu.cn) (S. Li), [w-li@zju.edu.cn](mailto:w-li@zju.edu.cn) (W. Li).

<https://doi.org/10.1016/j.apcatb.2019.01.049>

Received 30 August 2018; Received in revised form 3 January 2019; Accepted 17 January 2019

Available online 18 January 2019

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V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst and found that the CaCO<sub>3</sub> poisoned catalyst showed the lowest activity while CaSO<sub>4</sub> had the slightest influence. Kröcher [9] found that the acid sites were blocked by additive alkali metals occupying the non-atomic V<sub>2</sub>O<sub>5</sub> (010) sites, resulting in a strong deactivation of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst. Besides, the alkali metal poisoned Ce-Ti catalyst was learned by Du [10]. Experimental and theoretical results showed that the interaction of alkali metal atom with oxygen of CeO<sub>2</sub> and TiO<sub>2</sub> led to a deactivation. Fehrmann [11] compared the alkali resistance under different amount of copper doping on Cu/zeolite catalyst and optimized the content of copper species. At present, the deactivation by alkali metal was correlated to the drop of acid sites and reducibility of active species.

CuNbTi catalyst was proved to have a remarkable NO<sub>x</sub> conversion efficiency from our previous investigation [12]. However, its alkali resistance has not been studied. In this paper, we compared the poisoning effects of different alkali metals on CuNbTi catalyst. Commercial V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was also studied for comparison. And CuNbTi catalyst was found to exhibit a better anti-alkali property than VWTi catalyst in this work. Meanwhile, different alkali resistance and poisoning mechanisms between CuNbTi and VWTi catalysts under the same conditions were explored.

## 2. Experimental

### 2.1. Catalysts synthesis

The 0.8%Cu/Ti<sub>2</sub>NbO<sub>x</sub> catalyst was prepared by co-precipitation and wetness impregnation methods, which were described in detail in our previous publication [12]. The V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst with 1 wt% V<sub>2</sub>O<sub>5</sub> and 5 wt% WO<sub>3</sub> doping was synthesized by impregnation method. Ammonium metavanadate and ammonium paratungstate as precursors were dissolved in oxalic acid solution and deionized water, respectively. And then both of the solutions were mixed in a desired proportion. The P25 titania nanoparticles (Degussa, S<sub>BET</sub> = 55 m<sup>2</sup>/g, about 85% anatase and 15% rutile) were immersed in the mixture and kept in a rotary evaporator under 60 °C until water was removed. Afterwards, the prepared samples were dried at 110 °C for 8 h and calcined under 550 °C in air for 4 h. The 0.8%Cu/Ti<sub>2</sub>NbO<sub>x</sub> catalyst was labeled as CuNbTi while V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was denoted as VWTi for short hereafter.

The K<sub>2</sub>O-doped CuNbTi and VWTi catalysts with different mass ratio from 0.1 wt% to 2 wt% were also prepared by the incipient-wetness impregnating the CuNbTi and VWTi catalysts with KNO<sub>3</sub> aqueous solution. The mixture was firstly dipped in an ultrasonic generator for 30 min and magnetic stirring for 4 h. The residue obtained was dried at 85 °C overnight, followed by calcining in the air at 550 °C for 4 h. Meanwhile, different alkali metal oxides (K, Na, Mg, Ca) were loaded on CuNbTi catalysts with the same molar ratio by using the same method. NaNO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> were as the precursors. The poisoned catalysts were denoted as λM-CuNbTi and λM-VWTi, which λ represented the weight percentage (0–2.5%) of the alkali metal oxides and M was K<sub>2</sub>O, Na<sub>2</sub>O, MgO and CaO, respectively. All the samples were ground and sieved to 40–60 mesh for the performance evaluation.

### 2.2. SCR activity measurements

The steady-state NH<sub>3</sub>-SCR measurements were performed in a fixed-bed quartz tube reactor (inner diameter = 6 mm) with the outflow gases monitored by Nicolet iS50 FTIR spectrometer. The typical feed gas consisted of 500 ppm NH<sub>3</sub>, 500 ppm NO, 5 vol% O<sub>2</sub>, 5%–10% H<sub>2</sub>O (when used), 50–250 ppm SO<sub>2</sub> (when used) and N<sub>2</sub> as the balanced gas, with a total flow rate of 500 ml/min and a space velocity (GHSV) of 177,000 h<sup>-1</sup>. The SCR reaction was carried out between 175 °C and 500 °C under atmospheric pressure and the quartz tube was heated by a temperature-controlled furnace. About 0.15 g catalysts of 40–60 mesh were loaded between plugs of glass wool in the quartz tube and a K-type

thermocouple was insert to the catalyst bed to measure the reaction temperature. The effluent gas was kept throughout a heated gas cell (Pike Technologies, optical path length = 2.4 m), which was maintained at 110 °C during FTIR analysis. Initially the sample was activated with 10% O<sub>2</sub>/N<sub>2</sub> at 500 °C for 30 min to remove any possible adsorbed impurities and moisture. Afterwards, the catalyst was cooled down to room temperature and the reaction gas mixture was fed into the reactor. Each temperature was lasted 30 min for a steady state condition before collecting the spectrometer. The NO<sub>x</sub> (NO and NO<sub>2</sub>) conversion and N<sub>2</sub> selectivity were determined as follows:

$$NO_x \text{ conversion} = \frac{C_{NO_x(in)} - C_{NO_x(out)}}{C_{NO_x(in)}} \times 100\% \quad (1)$$

$$C_{NO_x} = C_{NO} + C_{NO_2} + 2C_{N_2O} \quad (2)$$

$$N_2 \text{ selectivity} = \left( 1 - \frac{2 \times C_{N_2O}}{C_{NO_x(in)} + C_{NH_3(in)} - C_{NO(out)} - C_{NO_2(out)} - C_{NH_3(out)}} \right) \times 100\% \quad (3)$$

### 2.3. Catalyst characterization

The surface morphology and structure of the catalyst were studied with a scanning electron microscopy S4800 at 15kv. N<sub>2</sub> adsorption-desorption experiments were carried out by a Micromeritics 3Flex instrument to investigate the textural characteristics of different catalysts. And the BET surface area was calculated using Brunauer-Emmett-Teller (BET) method in the relative pressure (P/P<sub>0</sub>) range of 0.05–0.30. X-ray diffraction (XRD) spectra were recorded at 0.02° intervals in the range of 10°–90° using X-ray diffractometer (PANalytical X' Pert PRO, Holland) equipped with a Cu-Kα (λ = 0.15406 nm, 40kv and 40 mA) radiation. Meanwhile, the atomic chemical state of catalyst was analyzed by an X-ray photoelectron spectroscopy (XPS) on Thermo Scientific Escalab 250Xi instrument using Al Kα (hν = 1486.6 eV) with a lower 10<sup>-7</sup> Pa base pressure. The pass energy was 30 eV and the catalyst was outgassed at room temperature before each test. Meanwhile, the obtained spectra were calibrated and standardized by carbon deposit C1 s peak at 284.6 eV. Electron paramagnetic resonance (EPR) spectra were determined using a Bruker A300 EPR Spectrometer with 0.2 mW microwave power in 110 K. Powder sample (about 20 mg) was contained in a quartz tube (OD = 1.5 mm) in each experiment. The center field was 3400 G and sweep width was 3000 G.

NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-TPD) experiments and temperature programmed reduction of hydrogen (H<sub>2</sub>-TPR) experiments were carried out on Micromeritics AutoChem II 2920. Prior to each experiment, 30 mg catalyst was placed in a quartz tube reactor and pretreated at 350 °C in a flow of high purified Helium (30 ml/min) for 1 h. Then the catalysts were cooled down to the room temperature in a flow of Helium. During each NH<sub>3</sub>-TPD experiment, the temperature was increased from 100 °C to 900 °C at a rate of 10 °C/min in Helium (30 ml/min) after reaching adsorption equilibrium in 10% NH<sub>3</sub>/He (30 ml/min) and purging with Helium for 2 h at 100 °C. The desorbed NH<sub>3</sub> signals were recorded by a quadrupole mass spectrometer (QIC-20). For the H<sub>2</sub>-TPR experiment, the sample was reduced in a mixture of 10% H<sub>2</sub>/Ar (30 ml/min) with the temperature increasing from 50 °C to 900 °C at a rate of 10 °C/min. And the signal was continuously monitored using a thermal conductivity detector (TCD) while the cold trap was used for eliminating the interference of H<sub>2</sub>O.

Pyridine adsorption infrared spectrum (Py-IR) were conducted using a Nicolet infrared spectrometer by accumulating 4000 scans with a resolution of 0.4 cm<sup>-1</sup>. The powder sample (about 10 mg) was pressed into a thin sheet and fixed into the sample cell. Then it was pretreated at 350 °C for 2 h under evacuation at a pressure of 1 × 10<sup>-3</sup> Pa. The pyridine was adsorbed at the room temperature followed by a temperature-programming to 200 °C and maintaining 30 min. The infrared spectra were collected after the sample was cooled down to the room

temperature.

In-situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) was collected in the range of 4000–650  $\text{cm}^{-1}$  on a Fourier transform infrared spectrometer (FTIR, Nicolet NEXUS 6700) equipped with a Harrick IR cell and an MCT/A detector cooled by liquid nitrogen. The spectral resolution was 4  $\text{cm}^{-1}$  with co-addition 64 scans. Before each test, the catalyst was heated up to 350  $^{\circ}\text{C}$  for 30 min in a flow of  $\text{N}_2$  to remove adsorbed impurities. The background in each target temperature was collected in the cooling process.

## 2.4. Theoretical calculation

All the theoretical calculations were based on the density functional theory (DFT). The potassium atom was selected as a probe to be located on the surface of CuNbTi catalyst for further elucidating the effect of alkali metal. And all the spin polarized calculations were carried out on the Vienna ab initio simulation package (VASP) [13] with the version of 5.4.1, which was a plane wave density functional code. For each calculation, the electron-electron exchange and correlation interactions were described by using the generalized gradient approximation (GGA) with the form of the Perdew-Burke-Ernzerhof (PBE) [14] functional. The projector augmented wave (PAW) [15] method was employed to describe the interaction between the core and valence electrons. The plane-waves basis was set with a cutoff energy of 400 eV. And the convergence criteria for the electronic self-consistent iteration and the ionic relaxation loop were set as the values of  $1 \times 10^{-5}$  eV and  $1 \times 10^{-4}$  eV/Å, respectively. Brillouin zone integrations were performed with k-point sampling using Monkhorst-Pack (MP) [16] of  $3 \times 3 \times 1$  for the models. The method of Gaussian smearing was employed to determine the valence electrons occupancies with a smearing width of 0.05 eV.

As the (101) crystallographic plane was preferred to expose in the CuNbTi catalyst, which has been proved in our previous work [12]. Anatase- $\text{TiO}_2$  (101) and anatase- $\text{Ti}_2\text{NbO}_x$  (101) surface with 4 atomic layers (two metal layers and two oxygen layers) of p ( $3 \times 1$ ) cell slab were prepared and cleaved, respectively. One thirds of titanium atoms were replaced by the niobium atoms in the model of  $\text{Ti}_2\text{NbO}_x$  support. The bottom two layers were fixed while the rest of two layers were fully relaxed. The dopant Nb were randomly distributed in the slab models. And the O-terminated surfaces were chosen and hydrogen-saturated because the massive OH groups were proved to exist in the results of FTIR (3.2.3 and 3.3). All the slabs models had the same vacuum space of more than 15 Å, which was large enough to avoid the interaction between periodical images.

The bonding energies ( $E_{B-\text{Cu}}$ ,  $E_{B-\text{K}}$  and  $E_{B-\text{NH}_3}$ ) were employed to evaluate the suitable site for Cu loading, K poisoning and  $\text{NH}_3$  adsorption. They were calculated as following expression:

$$E_{B-\text{CuorB-KorB-NH}_3} = E_{\text{total}} - E_{\text{slab}} - \frac{1}{n}E_{\text{bulk-Cuorbulk-Korbulk-NH}_3} \quad (4)$$

Where  $E_{\text{total}}$  was the total energy of the combined system with adsorbate copper loading on  $\text{Ti}_2\text{NbO}_x$  or  $\text{TiO}_2$  supporting slab, potassium atoms binding to the CuNbTi or CuTi catalyst slab and  $\text{NH}_3$  molecules adsorbing over CuTi or CuNbTi or KCuNbTi catalyst slab. And  $E_{\text{slab}}$  was the energy of slab before metal doping or  $\text{NH}_3$  adsorbing. Meanwhile,  $E_{\text{bulk-Cuorbulk-Korbulk-NH}_3}$  was the energy of bulk Cu or bulk K or bulk  $\text{NH}_3$  and  $n$  was the atom/molecule number of bulk Cu or bulk K or bulk  $\text{NH}_3$  (Cu = 4, K = 2 and  $\text{NH}_3$  = 1). In the K poisoning process, -OH group was also one of possible site, and it would be transformed to -OK group under K existence. Under this situation, the bonding energies were calculated as follows:

$$E_{B-K} = E_{\text{total}} - E_{\text{slab}} - \frac{1}{n}E_{\text{bulk-K}} + \frac{1}{2}E_{\text{H}_2} \quad (5)$$

Note that the adsorption energy was a negative value as the exothermic adsorption and the smaller value indicated a strong interaction between the adsorption substrate and adsorbate [17].

The rigorous energy convergence threshold with the value of  $10^{-7}$

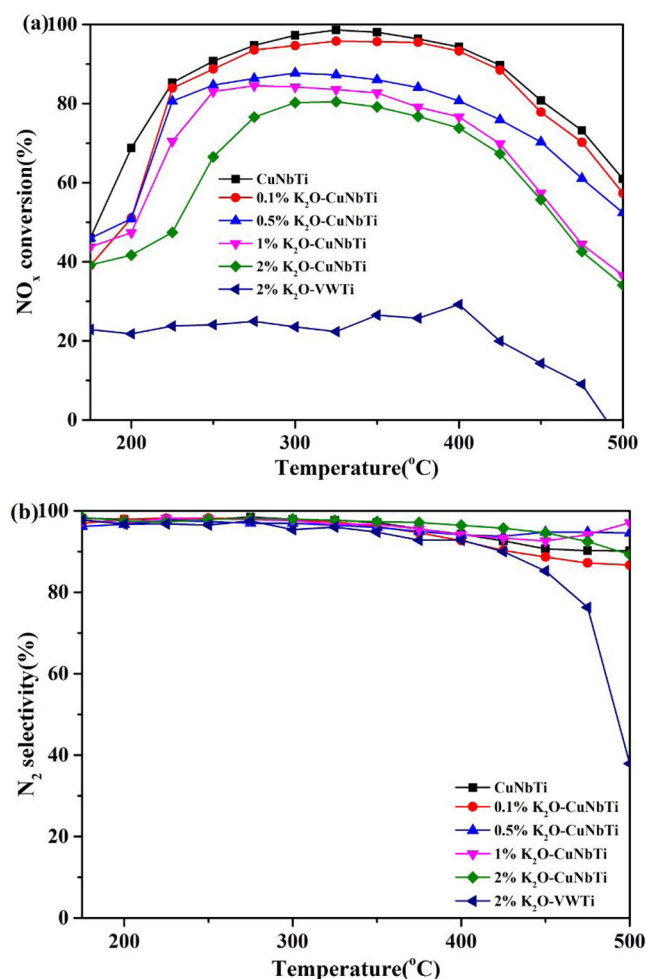


Fig. 1.  $\text{NO}_x$  conversion and  $\text{N}_2$  selectivity over: (a)-(b) different mass ratios of  $\text{K}_2\text{O}$ -loaded CuNbTi and VWTi catalysts and (c)-(d) different alkalis poisoning CuNbTi catalysts. Reaction conditions:  $[\text{NH}_3] = [\text{NO}_x] = 500$  ppm,  $[\text{O}_2] = 5\%$ ,  $[\text{H}_2\text{O}] = 5\%$ , total flow rate = 500  $\text{mL min}^{-1}$ , GHSV = 177,000  $\text{h}^{-1}$  and  $\text{N}_2$  as balance.

eV/unit cell was employed in vibrational calculations. Only surface O and OH were treated with 3 N degrees of freedom while the rest of the alloy surface was fixed during the vibrational calculations. All vibrations were treated as harmonic oscillator approximations.

## 3. Results and discussions

### 3.1. Catalytic activities

#### 3.1.1. Influence of $\text{K}_2\text{O}$ on $\text{NH}_3$ -SCR activity of CuNbTi and VWTi catalysts

The  $\text{DeNO}_x$  activities of  $\text{K}_2\text{O}$ -CuNbTi catalysts with different amount of  $\text{K}_2\text{O}$  doping were reported in Fig. 1(a) and (b) as a function of reaction temperatures. 5%  $\text{H}_2\text{O}$  was introduced in the feed stream within the whole reaction temperature for simulating the real exhaust condition. The SCR activity decreased gradually with the increase of  $\text{K}_2\text{O}$ . 0.1%-0.5%  $\text{K}_2\text{O}$  showed slight influences on the SCR activities between 250  $^{\circ}\text{C}$  and 400  $^{\circ}\text{C}$ . However, with 1% of  $\text{K}_2\text{O}$  loading, the  $\text{NO}_x$  conversion decreased to 82.69%–84.49% in the temperature range of 250–350  $^{\circ}\text{C}$  and the highest  $\text{NO}_x$  conversion decreased from 98.57% to 84.49%. Further increasing  $\text{K}_2\text{O}$  mass ratio to 2% resulted in a decrease of the highest  $\text{NO}_x$  conversion from 84.49% to 80.46%, with a volcano shape curve. Meanwhile, VWTi with 2%  $\text{K}_2\text{O}$  doping was synthesized for comparison. 2% $\text{K}_2\text{O}$ -VWTi catalyst showed about 20%  $\text{NO}_x$  conversion within the entire reaction temperature range. This indicated

that traditional VWTi catalyst with 2% K<sub>2</sub>O loading showed a considerable deactivation, which was consistent with previous researches [6]. As for N<sub>2</sub> selectivity, K<sub>2</sub>O poisoning CuNbTi catalysts exhibited a stable trend, since the N<sub>2</sub> selectivity was kept above 90% and N<sub>2</sub>O formation was only about 10 ppm over the whole reaction temperature range. However, the N<sub>2</sub> selectivity of 2%K<sub>2</sub>O-VWTi decreased gradually from 97.49% to 37.91% within 175–500 °C, while N<sub>2</sub>O production reached a highest value of 39 ppm. Notably, the experiment demonstrated that CuNbTi catalyst exhibited a great anti-K<sub>2</sub>O poisoning performance comparing with traditional VWTi catalyst. Meanwhile, the catalytic performance of aforementioned catalysts was tested without 5%H<sub>2</sub>O adding into the reaction mixture gas (as shown in Fig. 1S(a)–(b)). It showed that the extent of K<sub>2</sub>O poisoning became serious with the increase of doping amount, which was consistent with above results.

### 3.1.2. Influence of different alkalis on NH<sub>3</sub>-SCR performances of CuNbTi catalysts

The DeNO<sub>x</sub> performances of different alkalis poisoned CuNbTi catalysts were also tested with 5%H<sub>2</sub>O existing in the mixture gas and depicted in Fig. 1(c) and (d). The molar ratio of alkali atom over each catalyst was equal with potassium atom proportion in 2%K<sub>2</sub>O-CuNbTi (0.42 mmol/g). The mass fraction was 1.32%, 2.38%, 1.66% and 2% over Na<sub>2</sub>O-CuNbTi, CaO-CuNbTi, MgO-CuNbTi and K<sub>2</sub>O-CuNbTi samples, respectively. Different alkali oxides resulted in different poisoning degrees on its NH<sub>3</sub>-SCR activity. Addition of 1.66%MgO on the CuNbTi resulted in a decrease during the whole reaction temperature range, but more than 90% of NO<sub>x</sub> conversion was reached within the temperature range of 275–400 °C. 2.38% CaO-CuNbTi catalyst had a highest conversion of 91.04% at 350 °C, and the reaction temperature window over 90% NO<sub>x</sub> conversion shrunk to 325–400 °C. The presence of Na<sub>2</sub>O in the CuNbTi catalyst led to an obvious decline that the highest NO<sub>x</sub> conversion was only 82.39% at 325 °C. Meanwhile, Na<sub>2</sub>O-CuNbTi showed a similar behavior with K<sub>2</sub>O-CuNbTi on NO<sub>x</sub> conversion. However, the activity of 1.32%Na<sub>2</sub>O-CuNbTi was slightly higher than those of 2% K<sub>2</sub>O-CuNbTi. The addition of alkali had little effect on the N<sub>2</sub> selectivity and the value decreased slightly in the high temperature (400 °C–500 °C). Based on above findings, the poisoning degree of different alkali oxides on CuNbTi followed the order: K<sub>2</sub>O > Na<sub>2</sub>O > CaO > MgO. And this result was identical when 5% H<sub>2</sub>O was eliminated from the feed gas, as shown in Fig. 1S(c)–(d). Chen [6] proposed the similar observation about poisoning effects of different alkali oxides on traditional V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalysts in their study. Also, Tang [7] investigated the effect of sodium and calcium ions over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst while Du [10] studied the deactivation mechanism of sodium and calcium salts loading Ce/TiO<sub>2</sub> catalyst, both stating that the poisoning degree of sodium was severer than that of calcium. All of their investigations were consistent with our results. 2% K<sub>2</sub>O showed the most serious deactivation among all of equal molar alkali doping CuNbTi samples. Hence, 2%K<sub>2</sub>O-CuNbTi was selected for the following research and a comparison was made between 2%K<sub>2</sub>O-CuNbTi and 2%K<sub>2</sub>O-VWTi to present the different poisoning mechanisms.

### 3.1.3. The effect of H<sub>2</sub>O and/or SO<sub>2</sub> on NH<sub>3</sub>-SCR reaction

The effect of H<sub>2</sub>O and SO<sub>2</sub> on the NH<sub>3</sub>-SCR reaction was evaluated for further simulating the real exhaust condition. And the transient response experiments of H<sub>2</sub>O and/or SO<sub>2</sub> were conducted over 2%K<sub>2</sub>O-CuNbTi catalyst at 325 °C. As can be seen from Fig. 2(a), the NO<sub>x</sub> conversion of 2% K<sub>2</sub>O-CuNbTi catalyst was kept at about 74% before adding H<sub>2</sub>O. When 5%H<sub>2</sub>O was joined in the feed stream, the NO<sub>x</sub> conversion was kept stable at about 76% and N<sub>2</sub> selectivity was maintained 96%. Then the ratio of water vapor increased to 10%, and the NO<sub>x</sub> conversion and N<sub>2</sub> selectivity nearly maintained unchanged, indicating that the water vapor in flue gas did not result in any further poisoning for 2%K<sub>2</sub>O-CuNbTi catalyst.

SO<sub>2</sub> in the flue gas usually had a considerable negative influence on the activity of traditional VWTi or VMoTi catalyst and it had been proved that SO<sub>2</sub> would affect the alkali resistance of catalysts [18]. The fresh CuNbTi catalyst has been proved to exhibit an excellent sulfur resistance in our previous report [12]. Hence, the impact of SO<sub>2</sub> on 2% K<sub>2</sub>O-CuNbTi at 325 °C was investigated in this work and the corresponding results were presented in Fig. 2(b). The NH<sub>3</sub>-SCR reaction over 2%K<sub>2</sub>O-CuNbTi catalyst was kept stable for 1 h before SO<sub>2</sub> was added. The NO<sub>x</sub> conversion and N<sub>2</sub> selectivity kept 74% and 98%, respectively. When 50 ppm SO<sub>2</sub> was fed into the stream, NO<sub>x</sub> conversion decreased to 68% firstly and then increased to 76%. After that, 250 ppm SO<sub>2</sub> was added and the NO<sub>x</sub> conversion continued increasing to 79%. Meanwhile, the N<sub>2</sub> selectivity maintained above 97% within the entire reaction process. These results indicated that SO<sub>2</sub> improved the NO<sub>x</sub> conversion, which could be attributed to the enhanced surface acidity [19] and SO<sub>2</sub> did not pose the negative effect on the activity of 2%K<sub>2</sub>O-CuNbTi catalyst.

Fig. 2(c) showed the NO<sub>x</sub> conversion and N<sub>2</sub> selectivity of 2%K<sub>2</sub>O-CuNbTi catalyst under the coexistence of H<sub>2</sub>O and SO<sub>2</sub> at the reaction temperature of 325 °C. It was obvious that the coexistence of 5%H<sub>2</sub>O and 250 ppm SO<sub>2</sub> induced a decrease of the catalytic activity that the NO<sub>x</sub> conversion dropped from 74% to 64% while the N<sub>2</sub> selectivity decreased from 98% to 94%. It was commonly accepted that the loss of NH<sub>3</sub>-SCR activity was closely relevant with the formation and deposition of ammonium sulfate on the surface of catalyst during H<sub>2</sub>O and SO<sub>2</sub> coexisting in the feed stream [20,21]. After 5%H<sub>2</sub>O and 250 ppm SO<sub>2</sub> were cut off, the catalytic activity recovered gradually to some extent that NO<sub>x</sub> conversion kept about 69% and N<sub>2</sub> selectivity maintained 97%, which was lower than the initial value, suggesting the coexistence of H<sub>2</sub>O and SO<sub>2</sub> had an inhabitation effect on the 2%K<sub>2</sub>O-CuNbTi catalyst.

## 3.2. Physicochemical properties

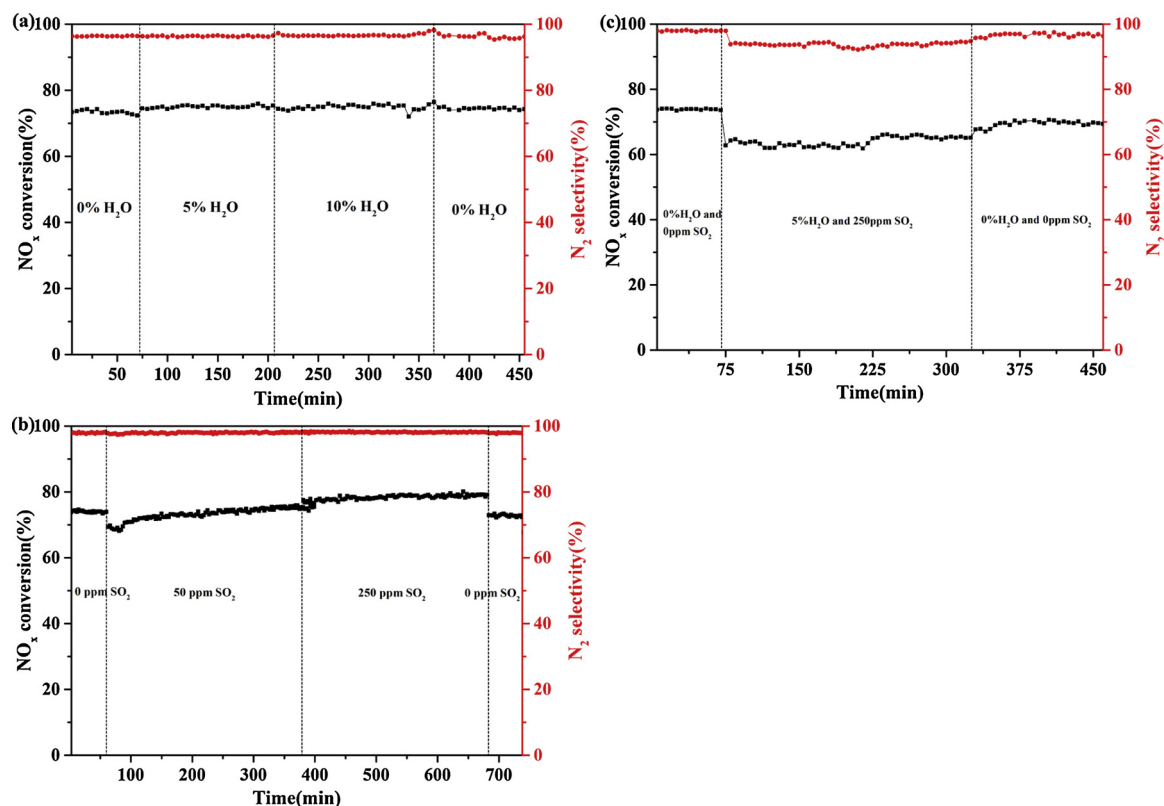
### 3.2.1. Morphological analysis

The representative SEM patterns of fresh and poisoned CuNbTi and VWTi catalysts were obtained to investigate the morphology change, as shown in Fig. 3S. It was remarkable that particle agglomerated after potassium loading on CuNbTi and VWTi catalysts. Compared with fresh catalysts, the potassium additive resulted in the active phase agglomeration over the surface of catalysts, which had a negative effect on the NH<sub>3</sub>-SCR activity [1]. Furthermore, the extent of agglomeration over 2%K<sub>2</sub>O-VWTi was severer than 2%K<sub>2</sub>O-CuNbTi. This might be related with that 2%K<sub>2</sub>O-VWTi catalyst was almost completely deactivated while 2%K<sub>2</sub>O-CuNbTi catalyst still exhibited 80% NO<sub>x</sub> conversion.

### 3.2.2. Textural characteristics

The microstructure characteristics of fresh and K<sub>2</sub>O-poisoned catalysts were firstly analyzed by using XRD patterns and the results were shown in Fig. 4S. All of the four samples mainly represented the anatase phase. Some rutile phase existed in VWTi and 2%K<sub>2</sub>O-VWTi catalysts, which was related to the support P25 TiO<sub>2</sub> containing 15% rutile TiO<sub>2</sub> phase. CuNbTi and 2%K<sub>2</sub>O-CuNbTi were well indexed to anatase TiO<sub>2</sub> (PDF-ICDD 99-0008) while VWTi and 2%K<sub>2</sub>O-VWTi were well indexed to anatase TiO<sub>2</sub> (PDF-ICDD 86-1157). Furthermore, the diffraction peaks of CuNbTi catalysts were broader and the peak intensities were weaker than those of VWTi catalysts, which was attributed to the function of Nb<sub>2</sub>O<sub>5</sub> on TiO<sub>2</sub> in the CuNbTi system [12]. Slight changes were observed and this proved that K<sub>2</sub>O doping did not alter the crystalline structure of CuNbTi and VWTi catalysts. In addition, the crystal particle sizes were calculated using Scherrer equation, as shown in Table 1. The grain sizes of CuNbTi and VWTi decreased from 9.3 nm and 27.4 nm to 9.0 nm and 26.3 nm, respectively. The smaller crystallite of K<sub>2</sub>O-poisoned catalysts indicated that loading of potassium oxides inhibited the grain growing, resulting in a drop of NO<sub>x</sub> conversion [5].





**Fig. 2.** Effect of (a)  $\text{H}_2\text{O}$ , (b)  $\text{SO}_2$ , (c)  $\text{H}_2\text{O}$  and  $\text{SO}_2$  on the  $\text{NH}_3$ -SCR activity of 2% $\text{K}_2\text{O}$ -CuNbTi catalyst at 325 °C. Reaction conditions:  $[\text{NH}_3] = [\text{NO}_x] = 500$  ppm,  $[\text{H}_2\text{O}] = 5\text{--}10\%$  (when used),  $[\text{SO}_2] = 50\text{--}250$  ppm (when used),  $[\text{O}_2] = 5\%$ , total flow rate =  $500 \text{ mL min}^{-1}$ , GHSV =  $177,000 \text{ h}^{-1}$  and  $\text{N}_2$  as balance.

The Brunauer-Emmett-Teller (BET) surface areas, total pore volume and average pore diameter of various catalysts were summarized in Table 1. The surface areas of CuNbTi and VWTi catalysts were  $73.1 \text{ m}^2/\text{g}$  and  $46.0 \text{ m}^2/\text{g}$  respectively while those of the  $\text{K}_2\text{O}$ -doped catalysts declined to  $69.3 \text{ m}^2/\text{g}$  and  $32.1 \text{ m}^2/\text{g}$ , respectively. This indicated that  $\text{K}_2\text{O}$  had a blocking or depositing effect on the sample [19]. Also, both the pore volume and diameter reduced obviously with  $\text{K}_2\text{O}$  loading on VWTi catalysts [8]. On the contrary, the  $\text{K}_2\text{O}$  poisoned CuNbTi catalyst showed a higher total pore volume ( $0.32 \text{ cm}^3/\text{g}$ ) and average pore diameter ( $16.9 \text{ nm}$ ) than the fresh CuNbTi catalyst ( $0.29 \text{ cm}^3/\text{g}$  and  $11.5 \text{ nm}$ ). Hence, the preservation of total pore volume and average pore diameter on 2% $\text{K}_2\text{O}$ -CuNbTi catalyst would be in favor of maintaining active sites for  $\text{NH}_3$ -SCR reaction. This supported the conclusion that 2% $\text{K}_2\text{O}$ -CuNbTi catalyst kept a well activity while 2%  $\text{K}_2\text{O}$ -VWTi deactivated completely.

The surface atom environment of the samples was investigated by XPS and the results were displayed in Fig. 3. Ti 2p, Nb 3d, Cu 2p and O 1s were analyzed and the main surface metal content was summarized in Table 2.

Fig. 3(a) displayed the spectra of Ti 2p with two binding energy of Ti  $2p_{1/2}$  and Ti  $2p_{3/2}$ . For CuNbTi and 2% $\text{K}_2\text{O}$ -CuNbTi, the peaks of Ti  $2p_{1/2}$  were located at  $464.70 \text{ eV}$  while the peaks of Ti  $2p_{3/2}$  were at  $458.97 \text{ eV}$ , which were the characteristics of  $\text{Ti}^{4+}$  species in anatase

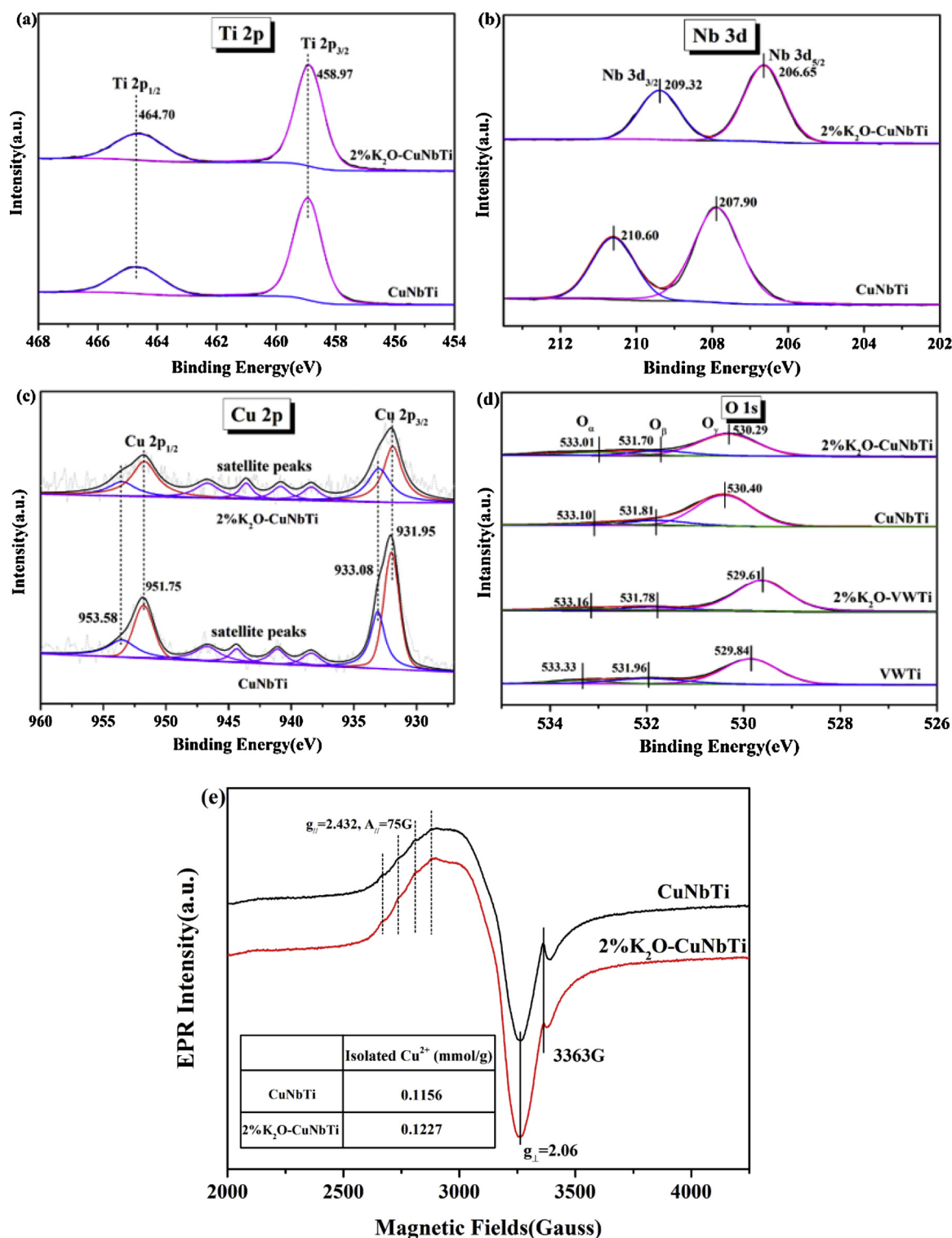
$\text{TiO}_2$  [21]. The binding energy kept nearly unchanged for the fresh and 2% $\text{K}_2\text{O}$  poisoned CuNbTi catalyst, illustrating that potassium had little influences on titanium of  $\text{Ti}_2\text{NbO}_x$  support.

The Nb 3d XPS spectra of CuNbTi and 2% $\text{K}_2\text{O}$ -CuNbTi were presented in Fig. 3(b), which were consisted of Nb  $3d_{3/2}$  and Nb  $3d_{5/2}$ . The peaks of Nb  $2p_{3/2}$  were located at  $210.60 \text{ eV}$  and  $209.32 \text{ eV}$  while the peaks of Nb  $2p_{5/2}$  were at  $207.90 \text{ eV}$  and  $206.65 \text{ eV}$  over CuNbTi and 2% $\text{K}_2\text{O}$ -CuNbTi catalyst, respectively. All of them were the characteristic peaks of  $\text{Nb}^{5+}$  species [22]. However, the existential status of  $\text{Nb}^{5+}$  species over CuNbTi catalyst was mainly  $\text{Nb}_2\text{O}_5$  [23] while  $\text{Nb}^{5+}$  existing in  $\text{KNbO}_3$  compound on the 2% $\text{K}_2\text{O}$ -CuNbTi catalyst [23,24]. It was obvious that the peaks of Nb 3d shifted to a lower binding energy after 2% $\text{K}_2\text{O}$  poisoned. The binding energy would change (shifted to a lower direction or a higher direction) when the density and arrangement of electron cloud transformed according to some literatures [25,26]. An increasing of electron cloud density would result in the binding energy shifting to a lower direction while the decreasing of electron cloud density was related to a higher direction offset [25]. And the formation of  $\text{KNbO}_3$  according to XPS results confirmed that  $\text{Nb}=\text{O}$  and  $\text{Nb}-\text{OH}$  were transformed to  $\text{Nb}-\text{O}-\text{K}$ , which enhanced the electron cloud arrangement of niobium atom and shifted the peaks to a lower binding energy direction. As a result, there was a fairly strong interaction between K and niobium species and K was trapped by  $\text{Ti}_2\text{NbO}_x$  support.

**Table 1**

BET surface area and pore parameters of catalysts measured by  $\text{N}_2$  adsorption experiments and particle size calculated by Scherrer equation from XRD experiments.

Samples	Surface area( $\text{m}^2/\text{g}$ )	Total pore volume( $\text{cm}^3/\text{g}$ )	Average pore diameter(nm)	Lattice parameter( $\text{\AA}$ )	Crystallite (nm)
CuNbTi	73.1	0.29	11.5	3.808	9.3
2% $\text{K}_2\text{O}$ -CuNbTi	69.3	0.32	16.9	3.796	9.0
VWTi	46.0	0.40	32.7	4.7091	27.4
2% $\text{K}_2\text{O}$ -VWTi	32.1	0.24	28.0	4.509	26.3



**Fig. 3.** The surface atom status and environment of fresh and 2%K<sub>2</sub>O poisoned catalysts: XPS spectra of (a) Ti 2p, (b) Nb 3d, (c) Cu 2p, (d) O 1s; And (e) EPR spectra of CuNbTi and 2%K<sub>2</sub>O-CuNbTi.

Copper species as active components were also scanned and the Cu 2p spectrum was shown in Fig. 3(c). There were mainly Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> corresponding to different kinds of copper and some satellite peaks existing between 935 eV and 950 eV, which were considered as bivalent copper species [21]. The Cu 2p<sub>3/2</sub> was fitted into two peaks at 931.95 eV and 933.08 eV, referred to Cu<sup>+</sup> species and Cu<sup>2+</sup>, respectively [27]. And the Cu 2p<sub>1/2</sub> was also split into two peaks located in 951.75 eV and 953.58 eV, which were ascribed to Cu<sup>+</sup> and Cu<sup>2+</sup>,

respectively [21]. Hence, the copper species mainly existed with two valence states over CuNbTi and 2%K<sub>2</sub>O-CuNbTi catalysts. It was widely accepted that the redox cycle between Cu<sup>2+</sup> and Cu<sup>+</sup> species played an important role in the activity of NH<sub>3</sub>-SCR over copper-based catalysts, and the appearance of Cu<sup>+</sup> species was proved to be related to the NO<sub>x</sub> reduction activity [28]. So, the relative content of Cu<sup>+</sup> / (Cu<sup>2+</sup> + Cu<sup>+</sup>) was calculated, as shown in Table 2. The Cu<sup>+</sup> species decreased (Cu<sup>2+</sup> increased) slightly after K<sub>2</sub>O was added, demonstrating that K<sub>2</sub>O had an

**Table 2**  
Main surface metal content of different samples.

samples	Atom concentration (%)						Atom ratio (%)	
	Ti	Nb	O	Cu	W	V	(O <sub>α</sub> + O <sub>β</sub> ) ratio	Cu <sup>+</sup> ratio
CuNbTi	18.73	10.84	69.05	1.37	–	–	25.85	48.03
2%K <sub>2</sub> O-CuNbTi	18.61	11.20	69.35	0.84	–	–	26.46	46.59
VWTi	29.29	–	65.24	–	3.55	1.92	28.12	–
2%K <sub>2</sub> O-VWTi	29.80	–	65.25	–	3.56	1.39	19.05	–

effect on the redox of Cu<sup>2+</sup> and Cu<sup>+</sup>.

NH<sub>3</sub>-SCR was a reaction with participation of oxygen and the surface active oxygen species were crucial to catalytic activity [29]. Hence, O 1s over the surface of catalyst was investigated and the results were shown in Fig. 3(d). The spectra demonstrated asymmetric peaks, which could be fitted into three bands with a primary band (O<sub>γ</sub>) and two sub-bands (O<sub>α</sub> and O<sub>β</sub>). Generally, the bands (O<sub>γ</sub>) at 529.61–530.40 eV corresponded to the lattice oxygen O<sup>2−</sup> [30–32]. And the ones (O<sub>β</sub>) at 531.70–531.96 eV could be assigned to surface chemisorbed oxygen species or ionization of oxygen species, such as OH<sup>−</sup>, O<sub>2</sub><sup>2−</sup>, O<sup>−</sup> and CO<sub>3</sub><sup>2−</sup> [19,33]. Another sub-bands (O<sub>α</sub>) at 533.01–533.33 eV were considered as the hydroxyl species (OH<sup>−</sup>) or adsorbed water [19,34]. Both of O<sub>α</sub> and O<sub>β</sub> belonged to surface active oxygen species due to their higher mobility, which were favored to the oxidation of NO to NO<sub>2</sub> and the redox circulation between active species of different valence states [19]. All of these impacts would facilitate to the process of NH<sub>3</sub>-SCR reaction. And then the relative ratio of (O<sub>α</sub> + O<sub>β</sub>) / (O<sub>α</sub> + O<sub>β</sub> + O<sub>γ</sub>) was quantified according to the O1s spectra, as shown in Table 2. The ratio of surface active oxygen over 2%K<sub>2</sub>O-VWTi was 19.05%, lower than that of VWTi (28.12%), revealing the restraining effects of K<sub>2</sub>O on the labile oxygen species in VWTi catalyst. Interestingly, 2%K<sub>2</sub>O-CuNbTi catalyst had a higher ratio (26.46%) than the fresh one (25.85%). The increase of labile oxygen over 2%K<sub>2</sub>O-CuNbTi contributed to maintain the catalytic performance of 2%K<sub>2</sub>O-CuNbTi catalyst. Compared with fresh CuNbTi and VWTi catalyst, the binding energy of O1s shifted to a lower direction for K<sub>2</sub>O poisoned catalyst, which was explained by the formation of chemical bonds between metal-dopant and active oxygen centers [35]. The poisoning element K increased the electron density among the valence shell of O atom. Some previous researches indicated that K could coordinate with both the vanadium and tungsten species, especially for the V=O, V–OH, W=O and W–OH on VWTi catalyst, forming V–O–K and W–O–K [8,36]. Meanwhile, K mainly interacted with Nb=O and Nb–OH and formed Nb–O–K over CuNbTi system. All of them would lead to an increase of

electron cloud density of O atom and an excursion towards lower direction for O1s peaks.

To further investigate the transformation of copper species, EPR analysis was applied to characterize isolated Cu<sup>2+</sup>, which was the only one to have EPR signals among all of the existence forms of copper species [37]. Isolated Cu<sup>2+</sup> has been proved to be the main active specie over CuNbTi catalyst in our previous researches. Fig. 3(e) presented the EPR profiles of fresh and 2%K<sub>2</sub>O poisoned CuNbTi catalysts. Both of them showed similar hyperfine structure with g<sub>∥</sub> = 2.432, A<sub>∥</sub> = 75 G and g<sub>⊥</sub> = 2.06, which represented the isolated Cu<sup>2+</sup> in anatase matrix [12]. Also, the peaks of 3363 G represented the support Ti<sub>2</sub>NbO<sub>x</sub> and it became weakened after K<sub>2</sub>O loading, indicating that K<sub>2</sub>O had an influence on the support, which was in accordance with the XPS results. Then the isolated Cu<sup>2+</sup> was quantified and the results were inserted in Fig. 3(e). 2%K<sub>2</sub>O-CuNbTi had a higher content of isolated Cu<sup>2+</sup> (0.1227 mmol/g) than CuNbTi (0.1156 mmol/g). The increment of isolated Cu<sup>2+</sup> after K<sub>2</sub>O loading was in agreement with the results of XPS. Therefore, the data of XPS and EPR indicated that K<sub>2</sub>O had an influence on Ti<sub>2</sub>NbO<sub>x</sub>, but the increasing content of isolated bivalent copper species maintained the NH<sub>3</sub>-SCR activity to some degrees over 2%K<sub>2</sub>O-CuNbTi catalyst.

### 3.2.3. Surface acidity

Surface acidity of fresh and K<sub>2</sub>O poisoned CuNbTi and VWTi catalysts were investigated using NH<sub>3</sub>-TPD methods and the curves were shown in Fig. 4(a). Meanwhile, in situ DRIFTS were performed to investigate the types of acid sites at different temperatures (Fig. 5). CuNbTi showed two peaks at 278 °C and 340 °C while 2%K<sub>2</sub>O-CuNbTi established two desorption peak at 204 °C and 283 °C. As for VWTi catalyst, three desorption peaks centered at 233 °C, 341 °C and 458 °C were detected, indicating abundant acid sites over VWTi catalyst. However, there was nearly no desorption peak for 2%K<sub>2</sub>O-VWTi catalyst. According to previous researches, the peaks below 300 °C were considered as the weakly chemisorbed NH<sub>3</sub> (weak and moderate acid sites) and the peaks under higher desorption temperature were regarded as the strongly chemisorbed NH<sub>3</sub>, namely strong acid sites [38]. Compared with fresh CuNbTi and VWTi catalysts, the total acid sites of 2%K<sub>2</sub>O poisoned samples declined apparently. 2%K<sub>2</sub>O-CuNbTi preserved the weak acid sites while 2%K<sub>2</sub>O-VWTi lost almost all of its acidity, which certified the favorable alkali resistance for CuNbTi catalyst.

Fig. 5 illustrated the results of in situ DRIFTS spectra of NH<sub>3</sub>-TPD over CuNbTi, 2%K<sub>2</sub>O-CuNbTi, VWTi and 2%K<sub>2</sub>O-VWTi catalysts. The negative bands at about 3679 cm<sup>−1</sup> for CuNbTi catalyst were assigned to the hydroxyl groups (Nb–OH) consumed during the process of NH<sub>3</sub> chemisorbing on the surface of catalyst to form NH<sub>4</sub><sup>+</sup> [30]. And the

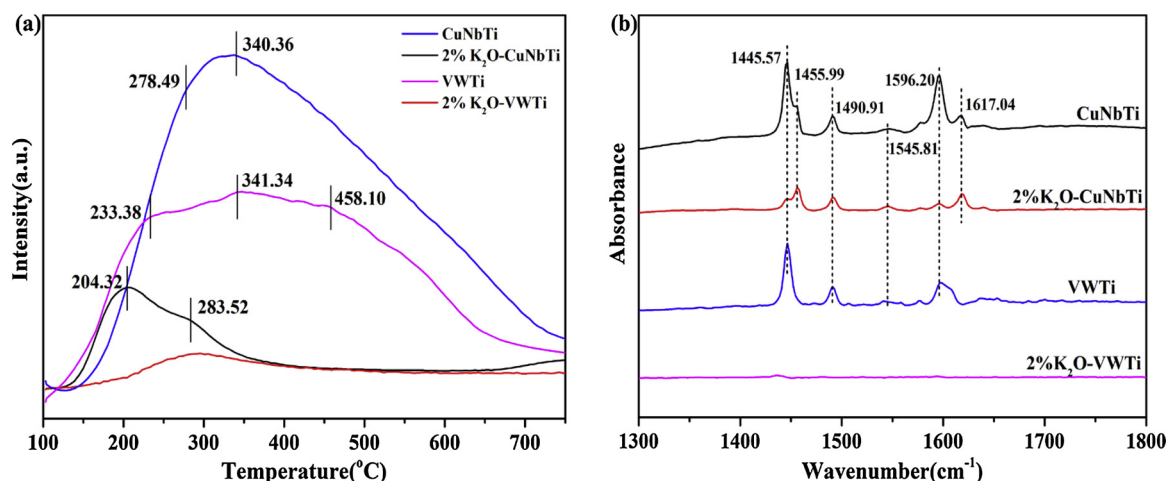


Fig. 4. (a) NH<sub>3</sub>-TPD and (b) Pyridine-IR profiles of fresh and K<sub>2</sub>O poisoned catalysts.

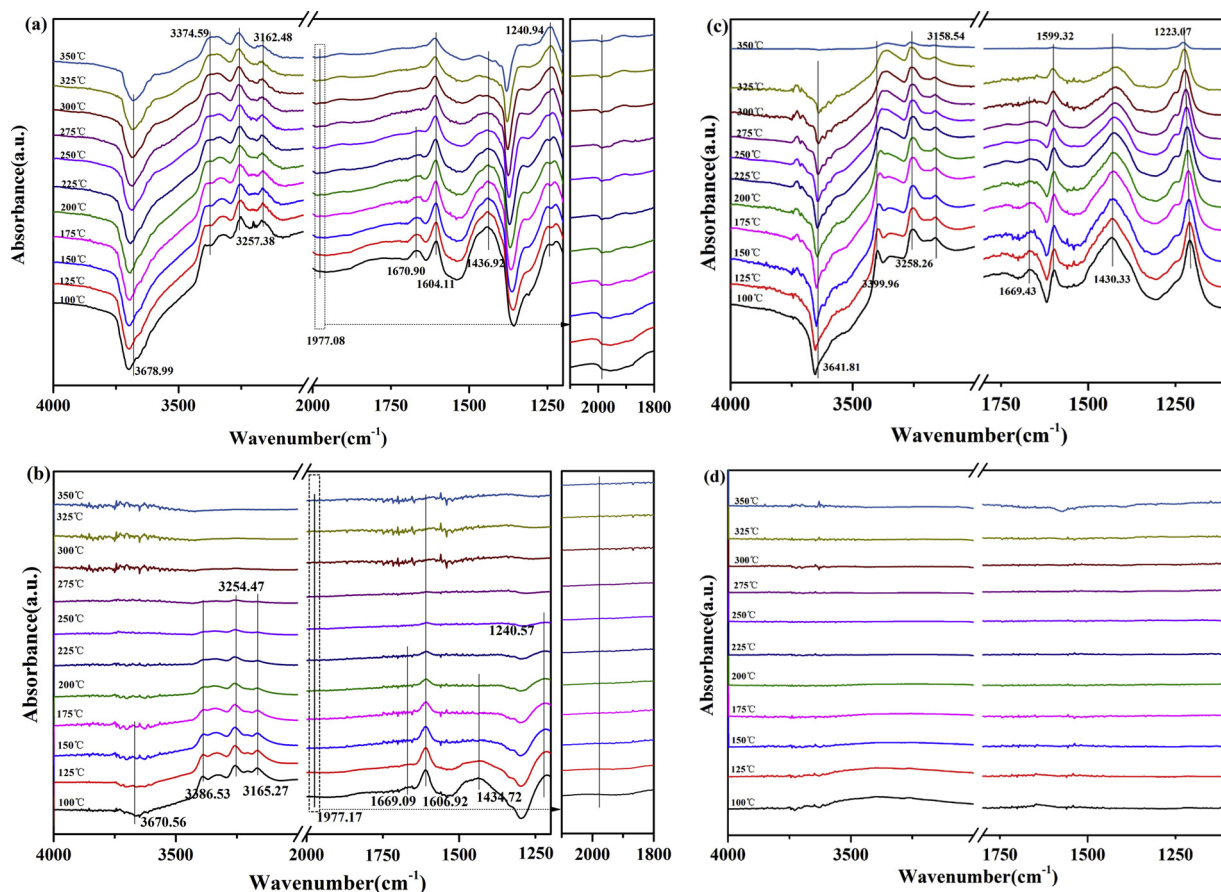


Fig. 5. in situ DRIFTS spectra of  $\text{NH}_3$  adsorption in 1000 ppm  $\text{NH}_3/\text{N}_2$  at 100 °C for 1 h and then purged with  $\text{N}_2$  before temperature programmed from 100 to 350 °C over (a) CuNbTi, (b) 2% $\text{K}_2\text{O}$ -CuNbTi (c) VWTi and (d) 2% $\text{K}_2\text{O}$ -VWTi catalysts.

$\text{Nb}=\text{O}$  corresponding to the band at  $1977\text{cm}^{-1}$  was also consumed during the  $\text{NH}_3$  adsorption [30]. Nevertheless, the bands representing  $\text{Nb}-\text{OH}$  became weakly at 100 °C and  $\text{Nb}=\text{O}$  vanished over 2% $\text{K}_2\text{O}$ -CuNbTi catalyst. This result declared that the presence of  $\text{K}_2\text{O}$  consumed  $\text{Nb}=\text{O}$  and  $\text{Nb}-\text{OH}$  over CuNbTi, leading to a decrease of surface acid sites. Also, the negative band at  $3642\text{cm}^{-1}$  for VWTi belonged to the consumption of  $\text{V}-\text{OH}$  [39]. Three bands at about  $3375\text{--}3399\text{cm}^{-1}$ ,  $3254\text{--}3258\text{cm}^{-1}$  and  $3158\text{--}3165\text{cm}^{-1}$  observed on CuNbTi, 2% $\text{K}_2\text{O}$ -CuNbTi and VWTi catalysts were attributed to the N–H stretching vibration modes coordinated  $\text{NH}_3$  [5,39]. The bands centered at approximately  $1600\text{--}1607\text{cm}^{-1}$  and  $1223\text{--}1241\text{cm}^{-1}$  could be ascribed to bending vibrations of N–H bonds in  $\text{NH}_3$  coordinately linked to Lewis acid sites [6,8,40], while the other peaks at  $1669\text{--}1771\text{cm}^{-1}$  and  $1430\text{--}1437\text{cm}^{-1}$  were assigned to bending vibrations of ionic  $\text{NH}_4^+$  on the Brønsted acid sites [32,41]. As for CuNbTi catalyst, the intensity of the bands at  $1669\text{--}1771\text{cm}^{-1}$  and  $1430\text{--}1437\text{cm}^{-1}$  reduced noticeably with the increase of temperature. On the contrary, the intensity of bands at  $1223\text{--}1241\text{cm}^{-1}$  decreased slightly and the bands at  $1600\text{--}1607\text{cm}^{-1}$  remained the same with the temperature rising from 100 °C to 350 °C. Hence, Lewis acid sites presented a better thermal stability than Brønsted acid sites. After doping 2% $\text{K}_2\text{O}$ , the bands corresponding to the  $\text{NH}_4^+$  on the Brønsted acid sites disappeared at 150 °C and the bands representing the N–H bonds coordinately linked to Lewis acid sites vanished gradually at 250 °C, suggesting that the presence of  $\text{K}_2\text{O}$  decreased the amount of acid sites and weakened the strength of acidity over CuNbTi. When compared to VWTi catalyst (as shown in Fig. 5(c)), all of the bands relating to Lewis and Brønsted acid sites declined gradually with the temperature increasing from 100 °C to 350 °C, showing a weaker acidity than CuNbTi catalyst. But 2% $\text{K}_2\text{O}$  loading resulted in the total loss of acid sites on

VWTi as no  $\text{NH}_3$  adsorption bands were existed in Fig. 5(d). According to the results of in situ DRIFTS, the peaks below 300 °C could be identified as  $\text{NH}_3$  desorption from most of Brønsted acid sites and some Lewis acid sites while the peaks higher 300 °C were caused by  $\text{NH}_3$  adsorption on Lewis acid sites.  $\text{NH}_3$  adsorption-desorption experiments proved that some acid sites were reserved for the 2% $\text{K}_2\text{O}$ -CuNbTi catalyst while no acid sites available for  $\text{NH}_3$  absorption over 2% $\text{K}_2\text{O}$ -VWTi catalyst.

The Pyridine-IR spectra of fresh and  $\text{K}_2\text{O}$  poisoned catalysts were shown in Fig. 4(b). CuNbTi and 2% $\text{K}_2\text{O}$ -CuNbTi showed similar bands. The bands at  $1445\text{cm}^{-1}$  and  $1596\text{cm}^{-1}$  on both CuNbTi and VWTi catalysts were ascribed to the Lewis acid sites while the bands of  $1456\text{cm}^{-1}$  and  $1617\text{cm}^{-1}$  only existing over the CuNbTi catalyst were also thought to be the Lewis acid sites [17]. And the rest bands at  $1491\text{cm}^{-1}$  and  $1546\text{cm}^{-1}$  for CuNbTi and VWTi catalysts were attributed to Brønsted acid sites [42]. The quantities of different acid sites were calculated and shown in Table 3. So, it could be concluded from the results of Pyridine-IR experiments that Lewis acid sites were the dominant acid sites over CuNbTi and VWTi catalyst. However, the total

Table 3

The quantities of different acid sites over fresh and  $\text{K}_2\text{O}$  poisoning catalysts.

	Brønsted acid sites( $\mu\text{mol/g}$ )	Lewis acid sites( $\mu\text{mol/g}$ )	Total acid sites( $\mu\text{mol/g}$ )	Brønsted/Lewis
CuNbTi	44.94	446.80	491.74	0.10
2% $\text{K}_2\text{O}$ -CuNbTi	24.56	143.75	168.31	0.17
VWTi	10.78	284.14	294.92	0.04
2% $\text{K}_2\text{O}$ -VWTi	3.08	3.43	6.51	0.90



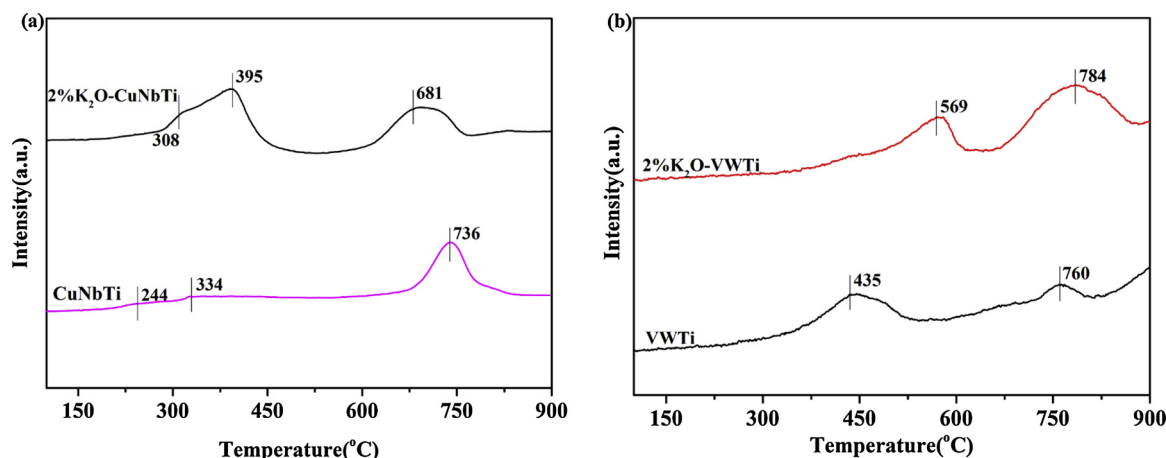


Fig. 6.  $H_2$ -TPR profiles of fresh and 2% $K_2O$  poisoned (a) CuNbTi and (b) VWTi catalysts.

acid sites on CuNbTi decreased from 491.74  $\mu\text{mol/g}$  to 168.31  $\mu\text{mol/g}$  after  $K_2O$  doping while it reduced from 294.92  $\mu\text{mol/g}$  to 6.51  $\mu\text{mol/g}$  after  $K_2O$  deactivated the VWTi catalyst. Obviously, 2% $K_2O$ -CuNbTi kept some acid sites although both of Lewis acid sites and Brønsted acid sites brought down to some extent, but 2% $K_2O$ -VWTi lost nearly all of its acid sites, which was in accordance with the results of  $NH_3$ -TPD and in situ DRIFTS. As a consequence, more acid sites on 2% $K_2O$ -CuNbTi than 2% $K_2O$ -VWTi contributed to its alkali-resistance.

### 3.2.4. Redox properties

$H_2$ -TPR was performed to characterize the redox properties of different catalysts and the results were reported in Fig. 6. In our previous studies, the isolated  $Cu^{2+}$  was reduced to  $Cu^+$  at 244 °C and then  $Cu^+$  was converted to copper metallic at 334 °C. The peaks at 736 °C were attributed to the reduction of  $Nb_2O_5$  to  $Nb_2O_4$ . For 2% $K_2O$ -CuNbTi (Fig. 6(a)), the reduction peak of  $Cu^{2+}$  to  $Cu^+$  and  $Cu^+$  to copper metallic shifted to 308 °C and 395 °C, respectively. The reduction temperature of copper increased after  $K_2O$  doping on CuNbTi catalyst, which suggested a drop in the reducibility of bivalent copper ions over 2% $K_2O$ -CuNbTi catalyst, resulting in a decrease of catalytic performance. As for the reduction temperature, both of physical texture and chemical property of catalyst would have an influence on the reducibility of active component. Delimaris [43] has proposed that the agglomeration of  $Cu_xCe_{1-x}$  catalyst led the low-temperature reduction peak of copper shifted to higher temperatures. The reduction peaks of  $V^{5+}$  to  $V^{3+}$  and  $W^{6+}$  to  $W^{4+}$  was proved to shift towards a higher temperature due to the coverage of alkali oxides over the surface of VWTi catalyst and the aggregation of bulk catalyst after alkali deactivating VWTi catalyst [44]. It was remarkable that particle agglomerated after potassium loading on CuNbTi catalyst according to SEM patterns and the surface area of 2% $K_2O$ -CuNbTi catalyst declined from 73.1  $\text{m}^2/\text{g}$  to 69.3  $\text{m}^2/\text{g}$  from  $N_2$ -physisorption experiment. These changes of physical texture might promote the reduction temperature of  $Cu^{2+}$  to  $Cu^+$  rising. On the other hand, the reduction temperature would also be affected by the chemical properties of catalyst [45,46]. The formation of  $CaWO_4$  could disrupt the interaction of  $V_2O_5$  and  $WO_3$  then lessen the reducibility of  $V^{5+}$  and  $W^{6+}$  species, leading to a higher reduction temperature over Ca-poisoned VWTi catalyst [8]. Also, Chen [36] attributed the increase of reduction temperature to the influence of Na and/or K on the chemical environment around V and W species over alkali-doped VWTi catalyst. As for 2% $K_2O$ -CuNbTi catalytic system, Bader Charge analysis was then conducted to further investigate the rise of reduction temperature for bivalent Cu over CuNbTi and 2% $K_2O$ -CuNbTi catalysts. And the results indicated that the charge distribution of copper over CuNbTi catalyst was 0.77 while it was 0.70 for 2% $K_2O$ -CuNbTi catalyst. After  $K_2O$  doping, the charge distribution of copper decreased from 0.77 to 0.70, indicating that the reducibility of copper

was weakened. This might explain the reduction temperature of  $Cu^{2+}$  to  $Cu^+$  shifting from 244 °C to 308 °C. In the meantime, the introduction of potassium and the transformation of  $KNbO_3$  produced an effect on the chemical environment of  $Cu^{2+}$  over 2% $K_2O$ -CuNbTi catalyst, which was another reason for the reduction temperature of  $Cu^{2+}$  to  $Cu^+$  rising.

The reduction peak of  $Nb_2O_5$  became broader and shifted to lower temperature from 736 °C to 681 °C, indicating that  $K_2O$  doping led to reduction of  $Nb_2O_5$  more easily. Additionally, it is commonly considered that the peak area or intensity reflected the consumption of hydrogen. And it was apparent that  $H_2$  consumption of  $Cu^{2+}$  for 2%  $K_2O$ -CuNbTi was much more than that for CuNbTi, indicating more  $Cu^{2+}$  existing over 2% $K_2O$ -CuNbTi catalyst, which was consistent with the results of XPS and EPR. More  $Cu^{2+}$  resulted in more  $H_2$  consumption during the temperature programmed reduction of hydrogen.

There were two reduction peaks over VWTi and 2% $K_2O$ -VWTi catalysts, as shown in Fig. 6(b). The first reduction peak at 435 °C on VWTi catalyst could be assigned to the reduction of  $V^{5+}$  to  $V^{3+}$  and  $W^{6+}$  to  $W^{4+}$  [4] while the high temperature peak at 760 °C belonged to the reduction of  $W^{6+}$  to  $W^{4+}$  [47]. Obviously, two peaks shifted to 569 °C and 784 °C after deactivation, respectively. So, 2% $K_2O$  severely suppressed the reducibility of active vanadia and tungsten oxide species. The  $H_2$  consumption decreased at 569 °C while the reduction peak for  $W^{4+}$  became larger, which was coincide with the results of previous researchers [29]. Thus, we could conclude that  $K_2O$  weakened the reducibility of vanadium species and damaged the interaction of vanadium species and tungsten species, which was essential for  $NH_3$ -SCR reaction [48].

### 3.3. Reaction mechanism

The synergistic promotional effect between copper species and niobium species over CuNbTi was proved to play a significant role in the catalytic activity in our previous investigations [12]. To further explore the synergistic mechanism in alkali resistance, 2% $K_2O$ -NbTi and 2% $K_2O$ -CuTi catalysts were also synthesized and the catalytic activity measurements were performed without 5% $H_2O$  existing in the simulating mixture gas. As shown in Fig. 2S, 2% $K_2O$ -NbTi deactivated among the whole range of reaction temperature, with less than 10.4%  $NO_x$  conversion and a maximum  $N_2$  selectivity of 85.3%. 2% $K_2O$ -CuTi exhibited a better activity than 2% $K_2O$ -NbTi, but the  $NO_x$  conversion only achieved 10%–23% in the temperature range of 300–425 °C. Whereas 2% $K_2O$ -CuNbTi showed the best activity since its maximum  $NO_x$  conversion was 73.8% while  $N_2$  selectivity remained above 85% in the whole temperature range.  $N_2$  selectivity of three catalysts was in the following sequence: 2% $K_2O$ -CuNbTi > 2% $K_2O$ -CuTi > 2% $K_2O$ -NbTi. Therefore, the synergistic promotional effect also existed in the process

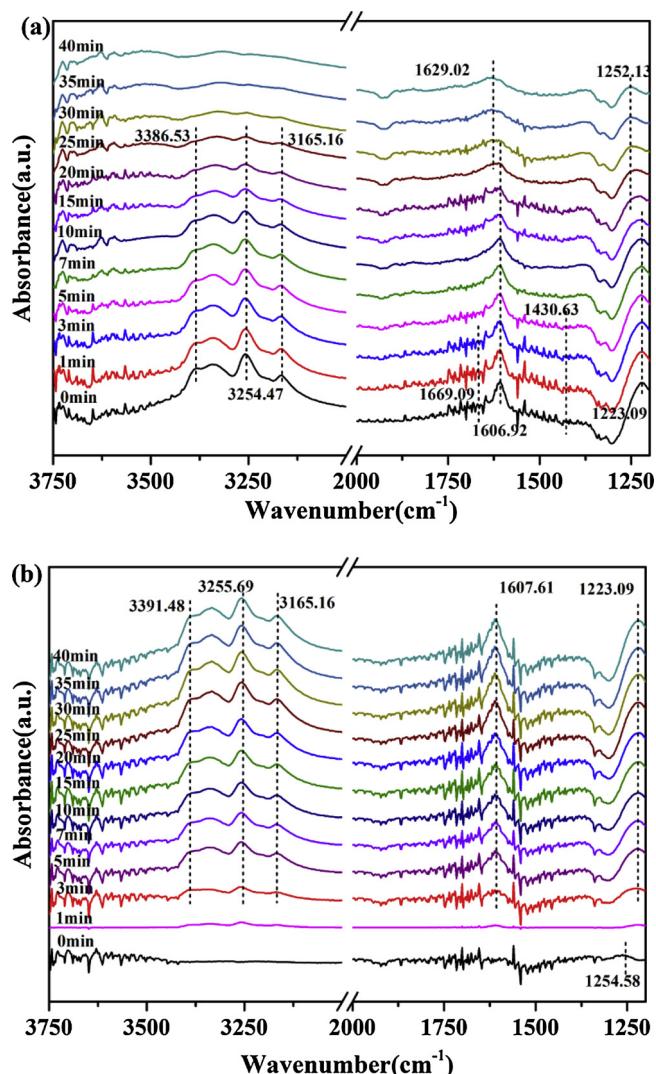


Fig. 7. in situ DRIFTS spectra of (a) gaseous NO and O<sub>2</sub> reacted with pre-adsorbed NH<sub>3</sub> species and (b) gaseous NH<sub>3</sub> and O<sub>2</sub> reacted with pre-adsorbed NO + O<sub>2</sub> species at 225 °C over 2%K<sub>2</sub>O-CuNbTi. Reaction conditions: [NH<sub>3</sub>] = 1000 ppm (when used), [NO] = 1000 ppm (when used), [O<sub>2</sub>] = 5%, total flow rate = 100 mL min<sup>-1</sup> and N<sub>2</sub> as balance.

of alkali resistance. The experiments' results in section 3.2 indicated that Ti<sub>2</sub>NbO<sub>x</sub> could trap K<sub>2</sub>O, protecting the active species of isolated Cu<sup>2+</sup> and that copper species preserved a certain amount of acid sites and active species over the surface of 2%K<sub>2</sub>O-CuNbTi catalyst for the NH<sub>3</sub>-SCR reaction.

Temperature programmed surface reaction was conducted using in situ DRIFTS at 225 °C to learn about the reaction mechanism. Firstly, the catalyst was exposed in 1000 ppm NH<sub>3</sub>/N<sub>2</sub> (100 ml/min) for 1 h to be saturated and then purged with N<sub>2</sub> (100 ml/min) for 30 min to eliminate physisorption NH<sub>3</sub>. After that, 1000 ppm NO/N<sub>2</sub> and 5% O<sub>2</sub> was introduced and the spectra were recorded as a function of time. As shown in Fig. 7(a), several bands at 3386 cm<sup>-1</sup>, 3254 cm<sup>-1</sup>, 3165 cm<sup>-1</sup> attributed to the N–H stretching vibration modes coordinated NH<sub>3</sub> and other bands at 1607 cm<sup>-1</sup>, 1223 cm<sup>-1</sup> assigned to the bending vibrations of N–H bonds in NH<sub>3</sub> coordinately on Lewis acid sites were detected after pre-adsorbed NH<sub>3</sub> following by N<sub>2</sub> purging. However, NH<sub>4</sub><sup>+</sup> on the Brønsted acid sites at the bands of 1670 cm<sup>-1</sup> and 1431 cm<sup>-1</sup> were not observed due to the weak stability at 225 °C, which could be verified by in situ DRIFTS of NH<sub>3</sub>-TPD. The surface NH<sub>3</sub> species were expended gradually after NO and O<sub>2</sub> introduction. At the same time, some new bands at 1629 cm<sup>-1</sup> and 1252 cm<sup>-1</sup> were

appeared at 25 min. For the band at 1629 cm<sup>-1</sup>, some researchers regarded the band at 1620 cm<sup>-1</sup> as the bridging nitrates [19,49] while others attributed it to the δ<sub>HOH</sub> vibration [8,50]. Combined with Fig. 7(b), the bands at 1620 cm<sup>-1</sup> did not arise after NO and O<sub>2</sub> adsorption with N<sub>2</sub> purging. So the band at 1620 cm<sup>-1</sup> in this study was ascribed to δ<sub>HOH</sub> vibration, confirming the formation of H<sub>2</sub>O. The band at 1252 cm<sup>-1</sup> was attributed to bidentate nitrate [5]. The reaction of NO and O<sub>2</sub> with pre-adsorbed NH<sub>3</sub> indicated that the reaction followed Eley-Rideal (E-R) mechanism over 2%K<sub>2</sub>O-CuNbTi at 225 °C. However, it was really different that only one nitrate (bidentate nitrate) generated over 2%K<sub>2</sub>O-CuNbTi catalyst while both monodentate nitrate and bridging nitrate emerged for CuNbTi catalyst, which was proved in previous research [12].

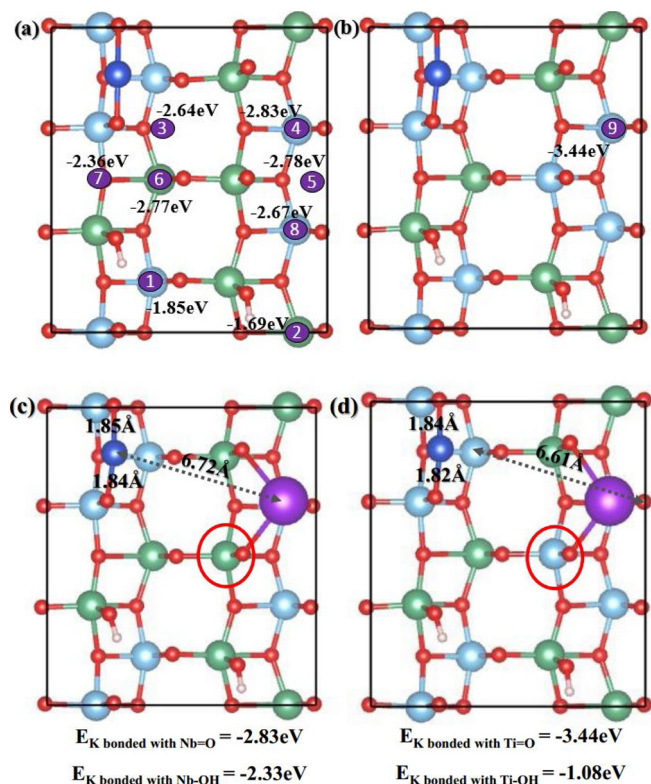
The reactivity of gaseous NH<sub>3</sub> and O<sub>2</sub> with pre-adsorbed NO + O<sub>2</sub> was also performed. After the activation under 350 °C for 30 min, the sample was cooled down to 225 °C. Then 1000 ppm NO (N<sub>2</sub> as balance) and 5% O<sub>2</sub> (by volume) were fed into the reactor for 1 h until adsorption saturation. Afterwards, the catalyst was purged with N<sub>2</sub> (1000 ml/min) for 30 min and then 1000 ppm NH<sub>3</sub> (N<sub>2</sub> as balance) with 5% O<sub>2</sub> (by volume) was introduced. The infrared spectra were collected at different time, as shown in Fig. 7(b). Only one band at 1255 cm<sup>-1</sup> (bidentate nitrate) was observed after NO and O<sub>2</sub> adsorption. The bidentate nitrate was consumed after 1 min and the NH<sub>3</sub> adsorbed species emerged at 3391 cm<sup>-1</sup>, 3256 cm<sup>-1</sup>, 3165 cm<sup>-1</sup>, 1608 cm<sup>-1</sup> and 1223 cm<sup>-1</sup>, indicating that the reaction over 2%K<sub>2</sub>O-CuNbTi followed Langmuir-Hinshelwood (H-L) mechanism at 225 °C. Besides, it was obvious that Eley-Rideal mechanism played a dominant role in the reaction process.

#### 3.4. Computational results

The geometric optimized structure of TiO<sub>2</sub> and Ti<sub>2</sub>NbO<sub>x</sub> was shown in Fig. 5S. In the model of Ti<sub>2</sub>NbO<sub>x</sub>, the ratio of titanium and niobium was 2/1 and niobium atoms replaced the sites of titanium atoms, which was consistent with our previous researching results [12]. Two different models of Ti<sub>2</sub>NbO<sub>x</sub> were selected as the main objects for the subsequence analysis (as shown in Fig. 5S(b)-(c)), which included all the possible adsorption sites for copper species. The valence state of Ti was +4 and Nb was +5 according to the Bader Charge analysis, which was consistent with the results of XPS in the previous work [12].

Then copper atoms were located on the surface of TiO<sub>2</sub> and Ti<sub>2</sub>NbO<sub>x</sub>, respectively. There were mainly two kinds of adsorption sites exposing, namely M=O and M–OH over the supports surface. Ti=O and Ti–OH were on the surface of TiO<sub>2</sub> while Ti=O, Ti–OH, Nb=O and Nb–OH existed over Ti<sub>2</sub>NbO<sub>x</sub>. All of the feasible supporting sites for Cu loading over Ti<sub>2</sub>NbO<sub>x</sub> were considered (as shown in Fig. 6S(a)-(b)) and the corresponding bonding energy (E<sub>B</sub>) was examined (as depicted in Table 1S). Terminal Ti=O and Nb=O exhibited a higher activity among all sites for copper supporting. And the bridging co-ordination showed a more stable molecular geometry among all the coordinating modes. Fig. 6S(c)-(e) presented three bridging modes with different E<sub>B</sub>. Obviously, the bonding energy of copper atom coordinating with two terminal oxygen atoms in O=Ti–O–Ti=O was –1.54 eV, which was the smallest value in all possible sites, indicating the most stable structure in this case. Meanwhile, the bonding energy of Nb–O–Cu–O–Nb (copper atom bonded with O=Nb–O–Nb=O) was –0.92 eV while it was –1.33 eV for Nb–O–Cu–O–Ti (copper atom coordinated with O=Nb–O–Ti=O), higher than that of Ti–O–Cu–O–Ti (copper atom coordinated with O=Ti–O–Ti=O). Compared with Nb=O, Ti=O exhibited a higher activity for copper linking to the surface of Ti<sub>2</sub>NbO<sub>x</sub> support. It was correlated with the liganacy of Ti<sup>4+</sup>, leading to unpaired electrons existing over the terminal Ti=O, which served as strong electron donor to bond with copper atom or hydrogen atom [17]. The bond length of Cu = O was in the range of 1.83 Å–1.86 Å.

To get insight into the alkali affinity for the CuNbTi catalyst, K atom



**Fig. 8.** (a)–(b) Possible sites for K locating at CuNbTi models and (c)–(d) the binding energy of K bonded with Nb = O, Nb-OH, Ti = O, and Ti-OH.  $\bullet$  represented Ti atom,  $\bullet$  represented Nb atom,  $\bullet$  represented Cu atom,  $\bullet$  represented H atom,  $\bullet$  represented O atom and  $\bullet$  represented the possible locating sites for K atoms.

was located on the surface of CuNbTi model. All the possible adsorption sites over the surface of Cu atom bonding with  $\text{O}=\text{Ti}-\text{O}-\text{Ti}=\text{O}$  in CuNbTi model were investigated and the binding energy ( $E_{B-K}$ ) was calculated in this computational experiment (Fig. 8(a)–(b)). The results of  $E_{B-K}$  suggested that K atom interacting with two  $\text{Ti}=\text{O}$  and one  $\text{Nb}=\text{O}$  simultaneously with  $-3.44 \text{ eV}$  adsorption energy displayed the most stable status. Furthermore, the exposed local structures of  $\text{Nb}=\text{O}$ ,  $\text{Nb}-\text{OH}$ ,  $\text{Ti}=\text{O}$ , and  $\text{Ti}-\text{OH}$  would dramatically affect the interaction between K atom and CuNbTi catalyst.

In order to reveal the K poisoning and selectivity mechanism, K binding energy on those four function sites was calculated, as shown in Fig. 8(c)–(d). Two K-poisoning slab models and four different clean slab models were employed according to the definition of K binding energy. For eliminating other effects and simplifying the analysis process, the same structure models were constructed, in which there is only one different site being replaced by those four functional sites (marked with red circle) on the surface. So the binding energy was solely determined by four different functional sites. After calculating, the binding energy of K atom with four functional sites followed an order:  $\text{Ti}-\text{OH}$  ( $-1.08 \text{ eV}$ ) >  $\text{Nb}-\text{OH}$  ( $-2.33 \text{ eV}$ ) >  $\text{Nb}=\text{O}$  ( $-2.83 \text{ eV}$ ) >  $\text{Ti}=\text{O}$  ( $-3.44 \text{ eV}$ ). Nevertheless, Cu atom and H atom preferentially expended  $\text{Ti}=\text{O}$  on the basis of the process of CuNbTi catalyst being synthesized. Thus  $\text{Nb}=\text{O}$  and  $\text{Nb}-\text{OH}$  would interacted with K atoms over the CuNbTi catalyst. And the formation of  $\text{KNbO}_3$  according to XPS results further confirmed the  $\text{Nb}=\text{O}$  and  $\text{Nb}-\text{OH}$  were transformed to  $\text{Nb}-\text{O}-\text{K}$ , which was consistent with this DFT calculation. Moreover, the bond length of  $\text{Cu}=\text{O}$  kept in the range of  $1.82 \text{ \AA}$ – $1.85 \text{ \AA}$  after K doping, indicating little effects of K on Cu. And the distance between Cu and K was  $6.61 \text{ \AA}$ – $6.72 \text{ \AA}$ .

Also, the structure of CuTi was built with the same method, as given in Fig. 7S. When CuTi catalyst was poisoned, the most stable structure

presented that K was close to Cu atom, interacting with bridging O, supporting O and terminal OH. The energy varied from  $-2.80 \text{ eV}$  to  $-0.28 \text{ eV}$  when K atom was close to and far from Cu atom, confirming the affinity of K for both copper unit and support phase with the former dominating. Compared with  $\text{KCuNbTi}$  catalyst, the distance between K atom and Cu atom over CuTi catalyst reduced from  $6.72 \text{ \AA}$  to  $4.14 \text{ \AA}$ . And the  $\text{Cu}=\text{O}$  distance of  $\text{KCuTi}$  was elongated from  $1.78 \text{ \AA}$  to  $1.80 \text{ \AA}$ – $1.83 \text{ \AA}$  with respect to the CuTi. Hence, potassium doping showed a remarkable perturbation of  $\text{Cu}=\text{O}$  in CuTi catalyst while it nearly maintained the initial  $\text{Cu}=\text{O}$  for CuNbTi catalyst, manifesting the protective effect of the support on the active component from being poisoned by alkali over CuNbTi catalytic system. Copper species and niobium species exhibited the synergistic promotional effect towards anti-alkali, which was coincided with the experiments results in 3.3.

In order to investigate the surface acidity of catalyst,  $\text{NH}_3$  was adsorbed on the fresh and K poisoned CuNbTi catalyst. The N atom in  $\text{NH}_3$  molecular coordinating with Cu atom represented the Lewis acid sites while N atom connecting the external hydroxyl denoted the Brønsted acid sites [51,52]. Cu acted as the Lewis acid sites and both of  $\text{Nb}-\text{OH}$  and  $\text{Ti}-\text{OH}$  served as the Brønsted acid sites for  $\text{NH}_3$  adsorption. When  $\text{NH}_3$  adsorbed on Cu of CuNbTi system, the effect of  $\text{Nb}=\text{O}$  around Cu was investigated, as shown in Fig. 9(a)–(c). The hydrogen of  $\text{NH}_3$  molecular would interact with contrapuntal oxygen in this case.  $\text{NH}_3$  molecular was adsorbed on Cu sites with two  $\text{Nb}=\text{O}$  around, exhibiting the most steady model with an adsorption energy of  $-1.10 \text{ eV}$ .  $\text{NH}_3$  could also adsorb on  $\text{Nb}-\text{OH}$  and  $\text{Ti}-\text{OH}$  with adsorption energy of  $-0.37 \text{ eV}$  and  $-0.16 \text{ eV}$  (shown in Fig. 9(d)–(e)), respectively. These results suggested that it was easier for  $\text{NH}_3$  adsorbing on Lewis acid sites than Brønsted acid sites. After K doping (Fig. 9(f)–(g)),  $\text{NH}_3$  adsorbed on Cu site with an adsorption energy of  $-0.62 \text{ eV}$  and the bond length of  $\text{H}-\text{O}$  increased from  $1.92 \text{ \AA}$  to  $2.02 \text{ \AA}$ . This indicated that K doping could weaken the interaction between hydrogen of  $\text{NH}_3$  molecular and contrapuntal oxygen in the catalyst, resulting in an increase of adsorption energy. Meanwhile, it was difficult for  $\text{NH}_3$  adsorbing on  $\text{Ti}-\text{OH}$  as the  $E_{\text{ads}}$  was just  $-0.03 \text{ eV}$ . The decrease of  $\text{NH}_3$  adsorption sites and increase of adsorption energy was one of the reasons for the catalytic activity reducing over  $\text{KCuNbTi}$  catalyst.

Besides, the experiment of  $\text{NH}_3$  adsorbing over  $\text{KCuTi}$  catalyst was also performed, as shown in Fig. 8S. The adsorption energy of  $\text{NH}_3$  adsorbing on Cu in  $\text{KCuTi}$  system was  $-0.72 \text{ eV}$ , higher than  $-1.10 \text{ eV}$  of  $\text{KCuNbTi}$ , illustrating that K had a stronger inhabiting effect on CuTi catalyst. And the length of  $\text{N}-\text{H}$  bond for  $\text{KCuTi}$  was  $1.71 \text{ \AA}$ – $1.91 \text{ \AA}$ , larger than that of free  $\text{NH}_3$  molecular ( $1.02 \text{ \AA}$ ) [52] while it kept nearly unchanged for  $\text{KCuNbTi}$  ( $1.02 \text{ \AA}$ ). The enlargement of  $\text{N}-\text{H}$  bond was related to the nonlocality of long pair electrons among the orbital of  $\text{NH}_3$ , which resulted in the migration of the electrons to Cu cation during the hybridization between  $\text{NH}_3$  molecular and Cu atom [52,53]. Thus, compared with  $\text{KCuTi}$ ,  $\text{Ti}_2\text{NbO}_x$  played an active role on  $\text{NH}_3$  adsorption over  $\text{KCuNbTi}$ , weakening the effect of potassium on  $\text{NH}_3$  adsorbing on the catalyst surface. To be concluded, potassium could be trapped by the  $\text{Ti}_2\text{NbO}_x$  support and the active copper species were protected over CuNbTi catalyst while potassium directly interacted with the copper on the CuTi catalyst and inhibited the activity of copper species and the adsorption of  $\text{NH}_3$  molecular. These revealed a synergistic effect of copper and niobium in the process of anti-alkali poisoning over CuNbTi catalyst. All of these results verified the conclusions of the experiments.

For the VWTi catalyst, K atoms interacted with both the active V atoms and the support  $\text{TiO}_2$  according to previous work and experimental results [4,54]. Therefore, alkali poisoning mechanisms were different for CuNbTi catalyst and VWTi catalyst. The active species of copper were protected in the CuNbTi catalyst while vanadium species were deactivated in the VWTi catalyst with potassium doping.



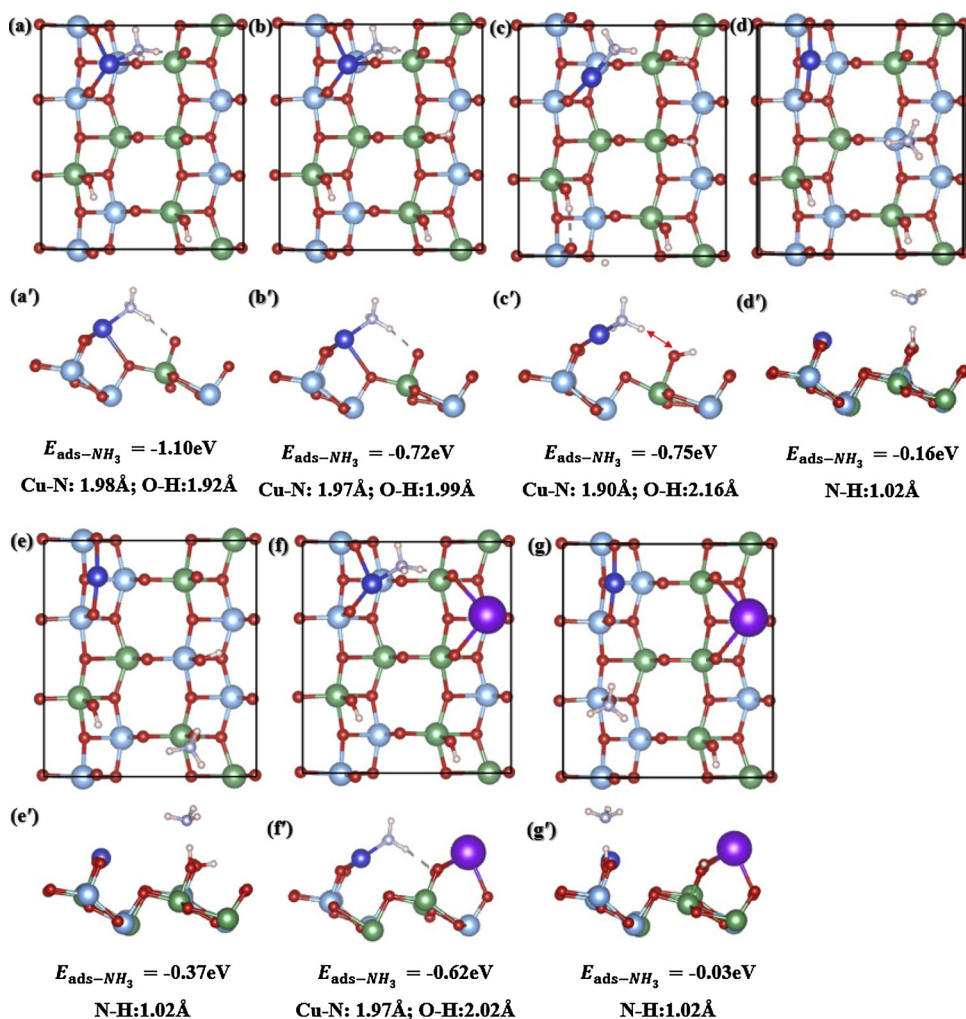


Fig. 9.  $\text{NH}_3$  adsorbed on (a)-(e) (a')-(e')  $\text{CuNbTi}$  and (f)-(g) (f')-(g')  $\text{KCuNbTi}$ : (a)-(g) top view and (a')-(g') side view.  $\text{Ti}$  atom,  $\text{Nb}$  atom,  $\text{Cu}$  atom,  $\text{K}$  atom,  $\text{N}$  atom,  $\text{H}$  atom, and  $\text{O}$  atom.

### 3.5. Discussions

All the results above demonstrated that  $\text{CuNbTi}$  catalyst exhibited greater alkali resistance than traditional  $\text{VWTi}$  catalyst. The poisoning mechanisms between  $\text{CuNbTi}$  and  $\text{VWTi}$  were really different, and the schematic models were shown in Fig. 10. A fundamental ion-exchange mechanism of  $\text{VWTi}$  deactivating by alkali was proposed that alkali metal ions reacted with protons from  $\text{V-OH}$  group, which was

Brønsted acid sites as the active phase for  $\text{NH}_3$ -SCR reaction in previous researches [55,56]. Both of Brønsted acid sites ( $\text{V-OH}$ ) and Lewis acid sites ( $\text{V=O}$ ) reduced significantly from the results of  $\text{NH}_3$ -TPD, Pyridine-IR and in situ DRIFTS in this work, which was the main reason for 2% $\text{K}_2\text{O}$ - $\text{VWTi}$  deactivation. The active vanadium species and support  $\text{TiO}_2$  were poisoned in the 2% $\text{K}_2\text{O}$ - $\text{VWTi}$  system. Besides, it could be observed that there was agglomeration over the surface of  $\text{VWTi}$  catalyst and both of the surface area and the total pore volume decreased

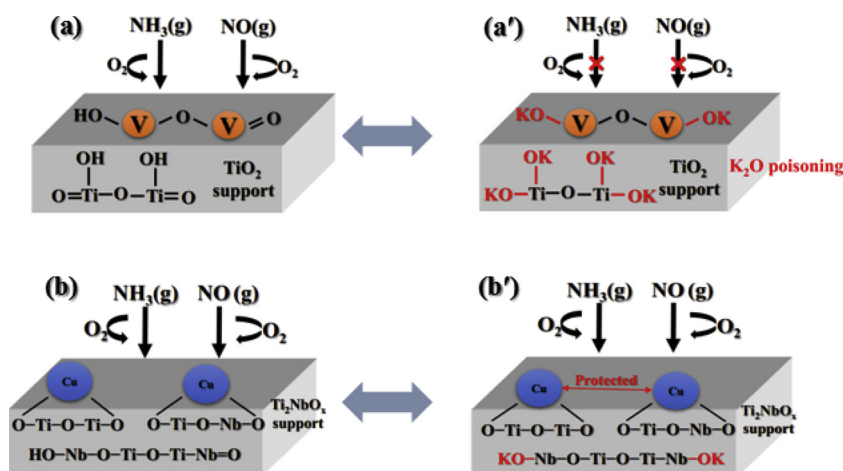


Fig. 10. Schematic model of 2% $\text{K}_2\text{O}$  poisoning  $\text{VWTi}$  and  $\text{CuNbTi}$  catalysts: (a) fresh  $\text{VWTi}$  (a') 2% $\text{K}_2\text{O}$ - $\text{VWTi}$  (b) fresh  $\text{CuNbTi}$  (b') 2% $\text{K}_2\text{O}$ - $\text{CuNbTi}$ .



after K<sub>2</sub>O doping. The surface active oxygen species over catalyst surface and the reducibility of 2%K<sub>2</sub>O-VWTi reduced. It was certified that alkali would affect the dispersion of vanadium and tungsten species on the surface of support, resulting in the decrease of surface active oxygen and reducibility, which was also important factors of catalytic activity [8]. The transformation of physical structure and chemical properties for 2%K<sub>2</sub>O-VWTi catalyst led to a deactivation. Nevertheless, the impact of K<sub>2</sub>O on CuNbTi catalyst was really different. The pore volume increased while the surface area dropped. And K atoms were preferable to coordinate with Nb–OH and Nb=O of the Ti<sub>2</sub>NbO<sub>x</sub> support, indicating a strong interaction of K<sub>2</sub>O with the support. This preserved enough surface chemisorbed active oxygen species and active isolated Cu<sup>2+</sup> for NH<sub>3</sub>-SCR reaction, although some structural changes existed due to the presence of K<sub>2</sub>O. Meanwhile, the interaction between K<sub>2</sub>O and Ti<sub>2</sub>NbO<sub>x</sub> support prevented the destruction of active copper species by K<sub>2</sub>O, and a certain amount of Brønsted acid sites and Lewis acid sites were reserved. And Ti<sub>2</sub>NbO<sub>x</sub> could also weaken the effect of potassium on NH<sub>3</sub> adsorption over KCuNbTi catalyst. Hence, 2%K<sub>2</sub>O-CuNbTi catalyst could still remain 80% NO<sub>x</sub> conversion efficiency. Niobium species and copper species were proved to present a synergistic role on the alkali resistance of CuNbTi catalyst. TiO<sub>2</sub> support with addition of niobium species trapped alkali K<sub>2</sub>O while the isolated Cu<sup>2+</sup> preserved remained the catalytic activity. And this work would provide a general strategy for developing novel anti-alkali poisoning NH<sub>3</sub>-SCR catalyst in the future.

#### 4. Conclusions

In this work, CuNbTi catalyst exhibited a better alkali resistance than traditional commercial VWTi catalyst. 2%K<sub>2</sub>O-CuNbTi achieved 80% NO<sub>x</sub> conversion at 325 °C while 2%K<sub>2</sub>O-VWTi was almost completely deactivated. K<sub>2</sub>O doping resulted in agglomeration of CuNbTi and VWTi catalysts, hence decreasing the surface area. However, the channels and pores of VWTi were deposited and blocked by K<sub>2</sub>O while the pores were preserved over CuNbTi catalyst, supplying active sites for the reaction. Meanwhile, K<sub>2</sub>O was more liable to coordinate with Nb–OH and Nb=O with a lower bonding energy of –2.33 eV––2.83 eV over the CuNbTi catalytic system according to the results of experiments and DFT calculations. K<sub>2</sub>O was trapped by Ti<sub>2</sub>NbO<sub>x</sub> support, forming KNbO<sub>3</sub> and protecting the active copper species from destruction to some extents. On the other side, 2%K<sub>2</sub>O caused the loss of all the acid sites on VWTi catalyst and suppressed the reducibility of active vanadia species, resulting in the deactivation. As for CuNbTi catalyst, 2%K<sub>2</sub>O also decreased the partial surface acid sites (especially strong acid sites) and declined the reducibility. However, the increase of isolated Cu<sup>2+</sup> as mainly active species maintained the catalytic activity. And TiO<sub>2</sub> with niobium modifying would weaken the influence of potassium on NH<sub>3</sub> adsorption over 2%K<sub>2</sub>O-CuNbTi catalyst. The synergistic effect between niobium species and copper species played an important role on resisting alkali poisoning. Besides, both Eley-Rideal (E-R) and Langmuir-Hinshelwood (H-L) mechanism occurred over 2%K<sub>2</sub>O-CuNbTi at 225 °C. The adsorbed NH<sub>3</sub> coordinated to the Lewis acid sites and bidentate nitrate were the dominating intermediate species during the NH<sub>3</sub>-SCR reaction procedure over 2% K<sub>2</sub>O-CuNbTi catalyst at 225 °C.

#### Acknowledgements

The authors thankfully acknowledge the financial support from the National Key Research and Development Program of China (No. 2017YFC0210904) and (No. 2017YFC0210403) and National Natural Science Foundation of China (NO. 21606195).

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the

online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.01.049>.

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**Update**

**Applied Catalysis B: Environmental**

Volume 271, Issue , 15 August 2020, Page

DOI: <https://doi.org/10.1016/j.apcatb.2019.03.018>



## Corrigendum

# Corrigendum to “The alkali resistance of CuNbTi catalyst for selective reduction of NO by NH<sub>3</sub>: A comparative investigation with VWTi catalyst” [Appl. Catal. B: Environ. 246 (2019) 166–179]

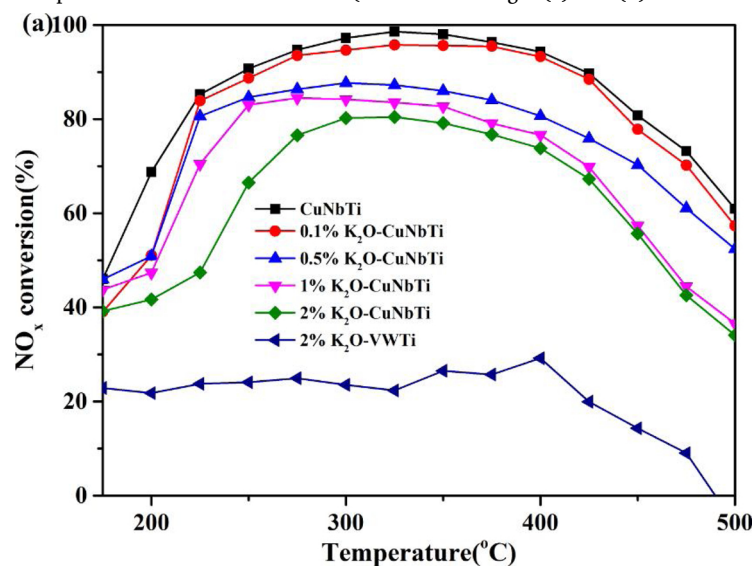
Xiaoxiang Wang<sup>a</sup>, Qiliang Cong<sup>a</sup>, Liang Chen<sup>a</sup>, Yun Shi<sup>b</sup>, Yao Shi<sup>a</sup>, Sujing Li<sup>a,\*</sup>, Wei Li<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Institute of Industrial Ecology and Environment, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

<sup>b</sup> Zhejiang University of Science & Technology, Hangzhou 310023, China

The authors regret to inform that figures and figure caption were wrongly published in the original article. Revised figures and caption are provided below:

(1) Figure 1 in the original manuscript should be revised as below. (There lacked Fig. 1(c) and (d) in the final edition.)



**Fig. 1** NO<sub>x</sub> conversion and N<sub>2</sub> selectivity over: (a)–(b) different mass ratios of K<sub>2</sub>O-loaded CuNbTi and VWTi catalysts and (c)–(d) different alkalis poisoning CuNbTi catalysts. Reaction conditions: [NH<sub>3</sub>] = [NO<sub>x</sub>] = 500 ppm, [O<sub>2</sub>] = 5%, [H<sub>2</sub>O] = 5%, total flow rate = 500 mL min<sup>−1</sup>, GHSV = 177,000 h<sup>−1</sup> and N<sub>2</sub> as balance.

(2) “O 1 s” should be revised to “O 1s” in the caption of Fig. 3.

(3) Figure 8 should be revised as below.

DOI of original article: <https://doi.org/10.1016/j.apcatb.2019.01.049>

\* Corresponding authors.

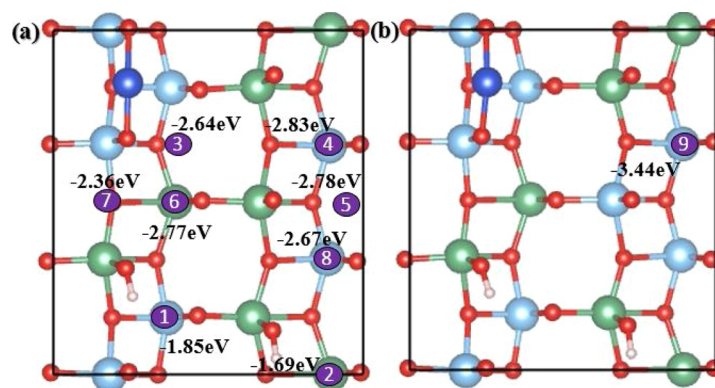
E-mail addresses: [sujing-li@zju.edu.cn](mailto:sujing-li@zju.edu.cn) (S. Li), [w\\_li@zju.edu.cn](mailto:w_li@zju.edu.cn) (W. Li).

<https://doi.org/10.1016/j.apcatb.2019.03.018>

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Please cite this article as: Xiaoxiang Wang, et al., Applied Catalysis B: Environmental, <https://doi.org/10.1016/j.apcatb.2019.03.018>





**Fig. 8** (a)–(b) Possible sites for K locating at CuNbTi models and (c)–(d) the binding energy of K bonded with Nb=O, Nb–OH, Ti=O, and Ti–OH. ● represented Ti atom, ● represented Nb atom, ● represented Cu atom, ● represented H atom, ● represented O atom and ● represented the possible locating sites for K atoms.

The authors would like to apologise for any inconvenience caused.